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RESEARCH PAPER RP1545

Part of Journal of Research of the National Bureau of Standards, Volume 31, July 1943

WIDTH AND SPACING OF TENSILE CRACKS IN AXIALLY REINFORCED CONCRETE CYLINDERS

By David Watstein and Douglas E. Parsons

ABSTRACT

In a study of the spacing and width of tensile cracks, axially reinforced cylinders were tested by applying tensile forces to the reinforcement and observing the deformations of the concrete and the spacing and the width of cracks. The test data and theoretical equations were in good agreement with respect to the effects of the principal factors controlling the spacing and the width of cracks. The spacing and the width of cracks were found to depend chiefly on the ratio of the diameter to the percentage of reinforcement and the nature of the deformations on the bars. It is concluded that the use of a type of reinforcement bar that will afford more reliable anchorage would result in better control of cracking of reinforced concrete and economy in the use of reinforcement steel.

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I. INTRODUCTION

The avoidance of large cracks is one of the important considerations in the design of reinforced-concrete structures. It is this consideration which accounts for the use, in some structures, of reinforcement in excess of that needed for strength. Although this practice may result in the prevention of wide cracks, the same objective may be attained, with more economical use of reinforcement steel, if use is made of all means of minimizing cracking.

This paper deals with the factors governing the spacing and width of cracks in symmetrically reinforced concrete members subjected to axial tension. Tests of axially reinforced concrete cylinders are described, and the results of the tests are compared with the indications of theory and with the results of previous investigations.

The bond strengths of the test bars were determined with a supplementary series of pull-out specimens.

II. MATERIALS

1. REINFORCEMENT BARS

The mechanical properties and the descriptions of the bars are given in table 1. The yield points were determined both by the "drop of the beam" and the "offset" methods, as described in ASTM Standards, Designation E 6–36.

TABLE 1.—*Mechanical properties of the reinforcement bars*

Description of reinforcement bars [1]	Nominal size	Diameter as determined on basis of weight per unit of length	Yield point	Tensile strength	Modulus of elasticity
	in.	*in.*	*lb./in.* [2]	*lb./in.* [2]	*lb./in.* [2]
One plain, hot-rolled	¾	0.87	39,000	61,000	29,000,000
One deformed	¾	.87	45,000	80,000	29,500,000
Two deformed	⅝	.62	47,000	75,000	29,000,000
One webbed, Isteg	no. 8	.95	[3] 76,000	----------	25,000,000
One threaded	¾	.80	[3] 75,000	80,000	25,000,000

[1] The reinforcement bars are illustrated in figure 1.

[3] "Offset" = 0.2 percent.

2. CONCRETE

Physical properties of the two different concrete mixes used in this study are given in table 2. The aggregates were Potomac River gravel and sand; the gravel ranged in size from no. 4 to ⅜ in.

The test specimens used in determining the tensile strength of the concrete were 4- by 16-in. plain concrete cylinders. The procedure of preparing and testing the tensile specimens was that developed at the National Bureau of Standards and described in reference [1a].[1]

TABLE 2.—*Physical properties of the concrete*

Designation	Proportions, by weight	Cement per cubic yard of concrete	Water per bag of cement	Slump	Compressive strength	Tensile strength, C_t	Modulus of elasticity in tension, E_t
		Bags	*gal.*	*in.*	*lb/in.*^{2}	*lb/in.*^{2}	*lb/in.*^{2}
"Weak"	1:3.4:3.6	5.4	9.5	2.5	[1] 2,900	[2] 250	2,900,000
"Strong"	1:1.5:2.0	9.6	5.0	2.0	[1] 5,300	[2] 450	3,800,000

[1] Average of 22 specimens.

[2] Average of 3 specimens.

[1] Figures in brackets indicate the literature references at the end of this paper.

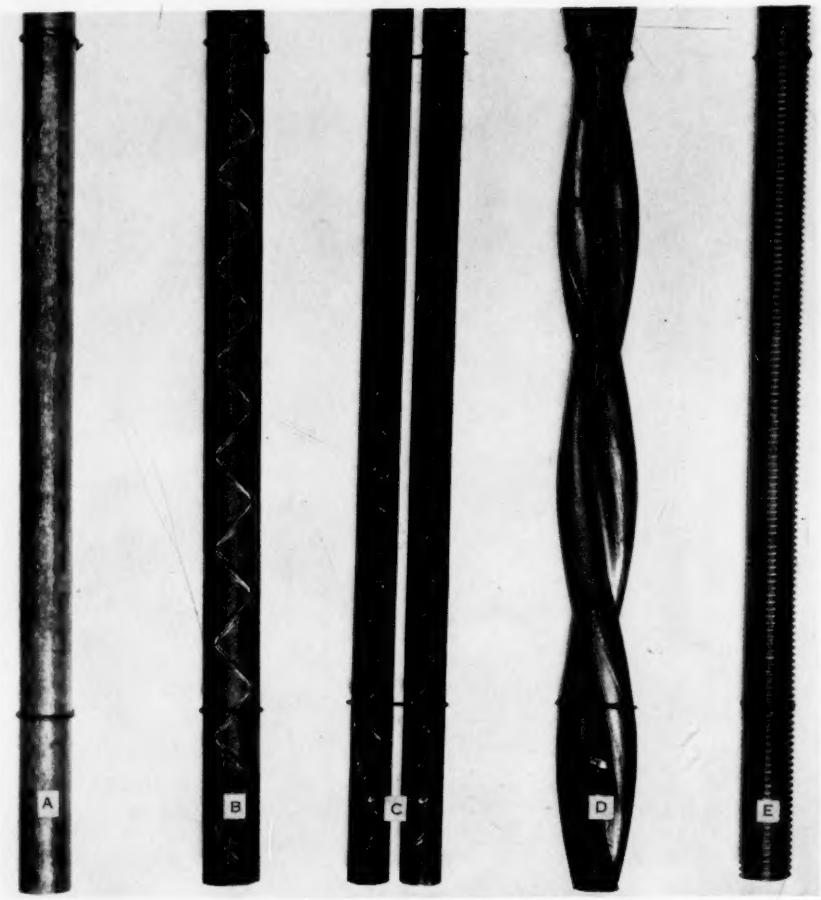

FIGURE 1.—*Reinforcement bars.*

A, ⅜-inch plain hot-rolled bar; *B*, ⅜-inch deformed bar; *C*, two ⅜-inch deformed bars; *D*, No. 8 webbed Isteg bar; *E*, ⅜-inch threaded bar.

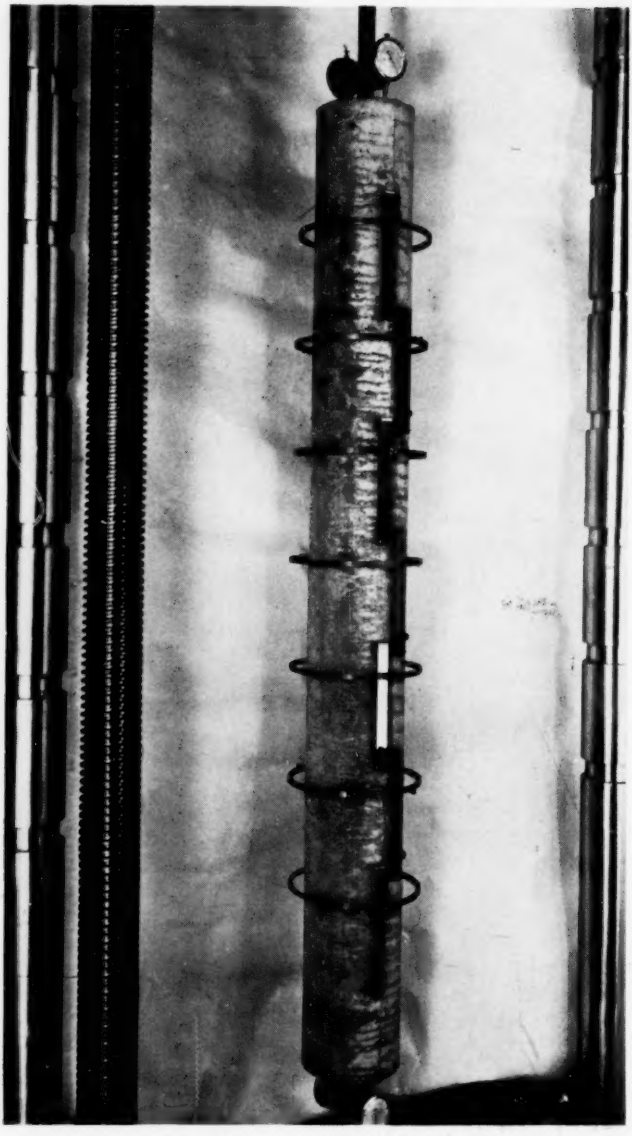

FIGURE 2.—*Reinforced-concrete cylinder in tension.*

III. REINFORCED TENSILE SPECIMENS

1. DESCRIPTION OF SPECIMENS AND STRAIN GAGES

The specimens for the measurement of widths and spacing of cracks were cylinders 4 ft long and 3½, 4, and 5 in. in diameter. They were reinforced with the five types of reinforcement bars shown in figure 1. The dimensions and percentages of reinforcement of the tensile cylinders are given in table 3; there were five similar cylinders corresponding to each type of specimen given in the table. The entire series of tests was made with both the "weak" and the "strong" concretes.

TABLE 3.—*Dimensions and percentages of reinforcement of the tensile specimens*

Diameter of concrete cylinder	Types of reinforcement bars				
	One ⅞ in. plain	One ⅞ in. deformed	Two ⅝ in. deformed	One No. 8 webbed Insteg	One ¾ in. threaded
	Percentage of reinforcement				
in.					
3½					5.2
4	4.8	4.8	4.9	5.7	4.0
5	2.9	2.9	3.0	3.5	2.4

The tensile strain on the surface of the test specimens and, subsequent to failure of concrete, the widths of tensile cracks were measured with fourteen 6-in. Tuckerman gages arranged in pairs along diametrically opposite lines. The elongation indicated by a pair of opposite strain gages bridging a given crack was taken as a measure of the width of the crack. Seven gages on each side of the specimen overlapped ½ in., thus covering a continuous length of 39 in. (see fig. 2). The gages bore on brass strips cemented to the surface of the concrete cylinders; the strips were ⅛ in. wide in the direction of the axis of the cylinder. Although the few cracks which appeared outside this gaged length were not measured, they were taken into account in estimating the average spacing of cracks.

The Tuckerman gages used in measuring the widths of cracks are highly sensitive and have a range of only 0.005 in.; consequently, they had to be reset several times during a test. While this was a disadvantage, the Tuckerman gages were selected, since they required no inserted gage points in the concrete, which might have produced objectionable planes of weakness in the concrete cylinders. Another advantage of the Tuckerman gages was the rapidity with which strain readings could be obtained.

2. METHOD OF TESTING

All reinforced tensile specimens were tested in a 60,000-lb capacity fluid-support, Bourdon-tube, hydraulic machine. The load was applied to the bar, which extended about 18 in. beyond each of the faces of the cylinder. In the case of specimens reinforced with a pair of ⅝-in. deformed bars spaced 2 in. apart, the load was applied to the threaded ends of the test bars through a 2- by 2- by 4-in. cross block,

which in turn was loaded by means of a threaded ⅞-in. bar passing through the center of the cross block.

An initial load of about 200 lb was applied and maintained while the gages were mounted on the specimen. The load was then applied in increments of about 2,000 lb until several tensile cracks were observed. Thereafter, the increments of load were increased to 3,000 or 4,000 lb, depending on the number of cracks and the expected maximum load.

In testing specimens with plain and deformed bars the load was applied up to the yield point of the steel; the threaded bars were stressed up to 60,000 lb/in.^{2}, and the somewhat larger webbed Isteg bars were stressed up to 50,000 lb/in.^{2}

IV. RESULTS OF THE TESTS AND DISCUSSION

1. WIDTHS OF TENSILE CRACKS

The graphs in figures 3 and 4 show the relation between widths of cracks and the corresponding stresses in the free ends of the reinforcing bars. The widths of cracks were proportional to the stress above the value designated as "the stress at zero width of crack," obtained by extrapolation. Most of the values of the crack widths plotted are the average values for five similar specimens for each type of bar. In several instances, the data represent fewer than five similar specimens, since those for several specimens were discarded in view of the uncertainty in strain gage readings or the erratic formation of tensile cracks.

Since the different test bars were not all of the same size, the effects of shape and surface roughness of bars on widths of cracks may be estimated more readily after adjusting these values for the differences in percentages of reinforcement. Accordingly, the data in figure 5 for the percentages of reinforcement shown were obtained from figure 3 and 4 by interpolation.

The graphs in figure 5 show that, for equal stresses in the steel, specimens reinforced with pairs of ⅝-in. deformed bars and those with threaded bars developed cracks of the smallest widths. At a stress of 30,000 lb/in.^{2}, the width of cracks in specimens with threaded bars were from 41 to 52 percent of the corresponding width in specimens reinforced with plain hot-rolled bars, whereas for the double ⅝-in. deformed bars this ratio ranged from 45 to 51 percent. At the same stress, the ratio of widths of cracks in specimens reinforced with double ⅝-in. deformed bars to corresponding values for ⅞-in. deformed bars ranged from 59 to 63 percent for "weak" concrete specimens and from 68 to 80 percent for specimens of "strong" concrete. The cross-sectional areas of a pair of ⅝-in. deformed bars and one ⅞-in. deformed bar were nearly equal, but the ratio of their perimeters was 0.70. There was no significant difference in the widths of cracks developed by specimens with ⅞-in. deformed bars and No. 8 webbed Isteg bars.

Referring again to figure 5, the stresses corresponding to a given width of crack were greater for the threaded and ⅝-in. deformed bars than for the others. In particular, for the width of crack in specimens reinforced with plain hot-rolled bars carrying a stress of 20,000 lb/in.^{2}, the stresses in the other bars were, on the average, 24,000 lb/in.^{2} with the Isteg bars, 25,000 lb/in.^{2} with the ⅞-in deformed bars and 35,000 lb/in.^{2} with the threaded and the ⅝-in. deformed bars.

Comparison of the results obtained with the "weak" and the "strong" concretes indicate no appreciable difference in the width of cracks for stresses in the reinforcement corresponding to commonly used design values. It was also observed that the relative standing

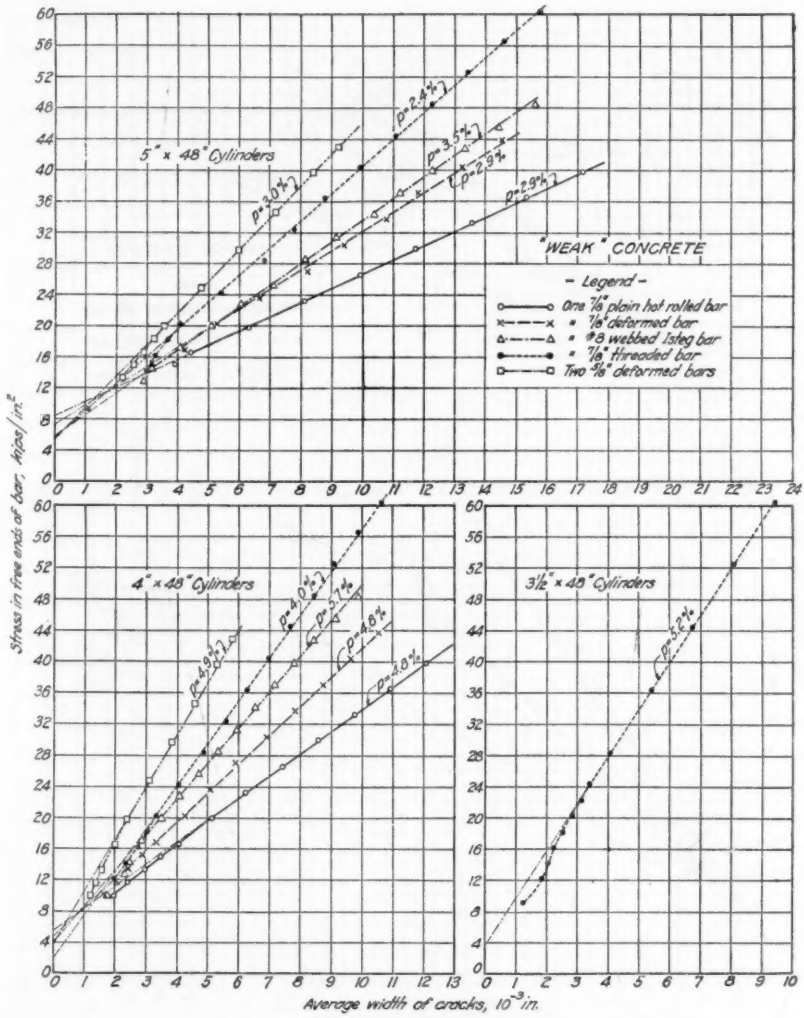
5" x 48" Cylinders
4" x 48" Cylinders
3½" x 48" Cylinders
"WEAK" CONCRETE
- Legend -
One ⅞" plain hot rolled bar
" ⅞" deformed bar
" #8 webbed Isteg bar
" ⅞" threaded bar
Two ⅞" deformed bars
Stress in free ends of bar, kips/in.²
Average width of cracks, 10⁻³ in.

FIGURE 3.—*Widths of tensile cracks observed in reinforced cylinders of "weak" concrete.*

1 kip=1,000 lb; p=percentage of reinforcement.

of the various types of bars remained substantially the same for the two concretes.

Several 4- and 5-in. cylinders of "weak" concrete, each reinforced with a smooth, cold-rolled steel bar, were tested (the data are not given in detail). The 4-in. cylinders developed one crack each, while the 5-in. cylinders did not crack when the steel was stressed to 60,000

lb/in.^{2} Unlike the cracks in other specimens, the width of cracks for cold-rolled bars did not vary linearly with the stress in the steel; rather, the rate of widening of the cracks with load became smaller as the stress in the steel increased. Measurements on the surface of the

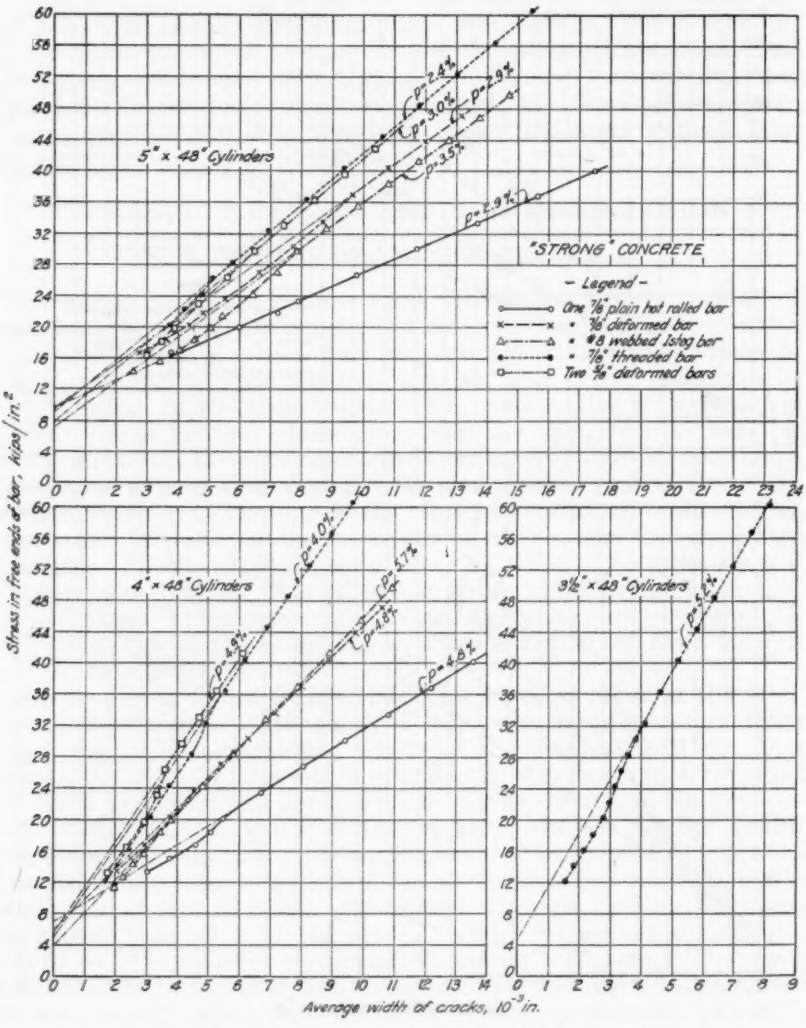
5" x 48" Cylinders
"STRONG" CONCRETE
- Legend -
One ⅞" plain hot rolled bar
⅞" deformed bar
#8 webbed Isteg bar
⅞" threaded bar
Two ⅝" deformed bars
4" x 48" Cylinders
3½" x 48" Cylinders
Stress in free ends of bar, kips/in.²
Average width of cracks, 10⁻³ in.

FIGURE 4.—*Widths of tensile cracks observed in reinforced cylinders of "strong" concrete.*

1 kip=1,000 lb; p=percentage of reinforcement.

5- by 48-in. uncracked cylinders indicated a sharply defined maximum tensile strain at a stress of about 16,000 lb/in.^{2}; as the stress in the steel was further increased, the tensile strain in the concrete began to fall off rapidly.

The observed behavior of the cold-rolled bar points to progressive break-down of bond as the stress in the steel increases; that is, the

bond is first destroyed at the point where the bar enters the concrete and as the stress increases the break-down of bond progresses along the reinforcement until the bond is practically destroyed along the entire embedded bar. This interpretation of the results is in agree-

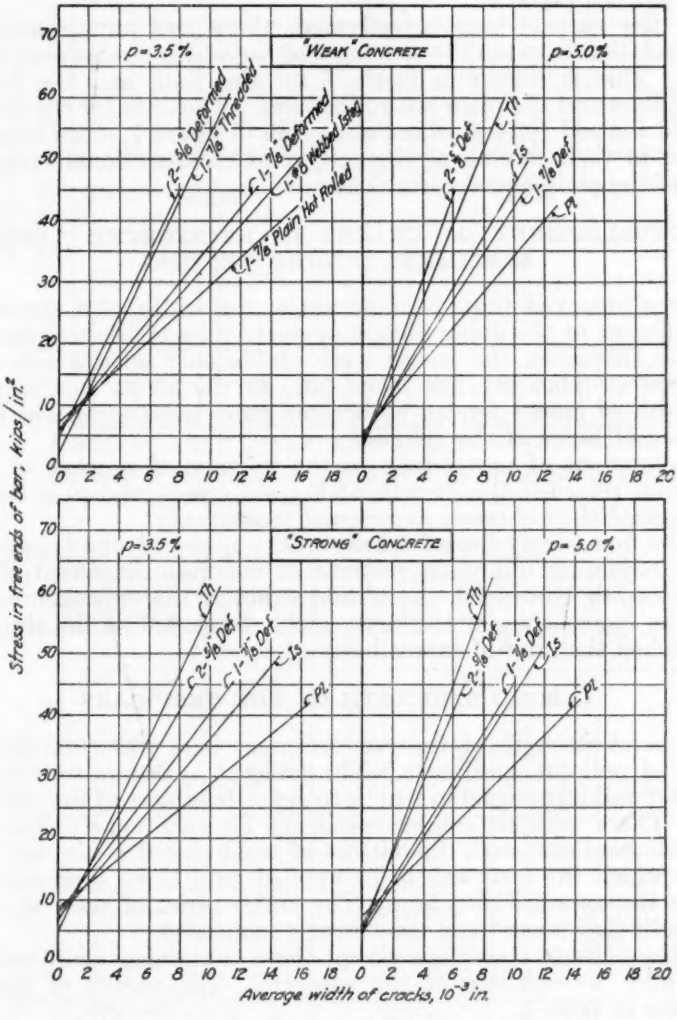

FIGURE 5.—*Widths of tensile cracks interpolated to correspond to cylinders with reinforcement of 3.5 and 5.0 percent.*

1 kip=1,000 lb.

ment with data on tests of smooth steel embedded in pull-out specimens reported by Glanville [1], Watstein [2], and Gilkey, et al. [3]. Gilkey, in particular, observed that in 48-in. pull-out specimens the bond stress at the loaded end of the bar began to decrease before there was any stress in the steel at a point 12 in. from the loaded end.

2. SPACING OF CRACKS

The spacing of cracks for the five types of bars in specimens of both "weak" and "strong" concrete is shown in figure 6, adjusted by interpolation to correspond to specimens having reinforcement of 3.5 and 5.0 percent.

For the various bars investigated, there was an approximately linear relation between the spacing and the width of cracks at a given stress. This is shown in figure 7 for the ⅝-in. and the ¾-in. deformed bars and the plain hot-rolled bars. The data for the threaded and the webbed Isteg bars are not given in figure 7, since these bars differed in their moduli of elasticity and cross-sectional areas from those of the plain and deformed bars.

3. DEVELOPMENT OF CRACKS IN REINFORCED TENSILE SPECIMENS DURING TESTING

It was observed that, in most cases, the width of a given crack was different at the diametrically opposite sides of the test specimen. In some instances, the cracks were visible only on one side of the cylinders at relatively low loads but, as the stress was increased, the width of cracks tended to become more nearly uniform around the circumference of the cylinder.

Development of new cracks in the vicinity of a crack of earlier formation retarded the growth of the old crack, and in some cases even caused the old crack to contract temporarily.

As the first widely spaced tensile cracks appeared, the tensile strain in the adjoining unbroken sections of concrete decreased sharply; as the loading continued, the tensile strain in the unbroken concrete began to increase again and new cracks developed as the elongation approached the limit of extensibility of concrete.

4. BOND STRENGTH OF THE TEST BARS

The bond strength of the reinforcement bars was determined by means of pull-out specimens. The pull-out cylinders were 6 in. in diameter and were equal in length to eight diameters of the embedded bars. There were six similar specimens for each type of bar, three of which were cast with the bottom of mold placed at the end of the bar to which the load was to be applied, and three specimens were cast in the opposite direction. The entire series of tests was made with both the "weak" and the "strong" concretes.

All the pull-out specimens except those containing plain hot-rolled steel failed by splitting of the concrete. The results of the tests are given in table 4.

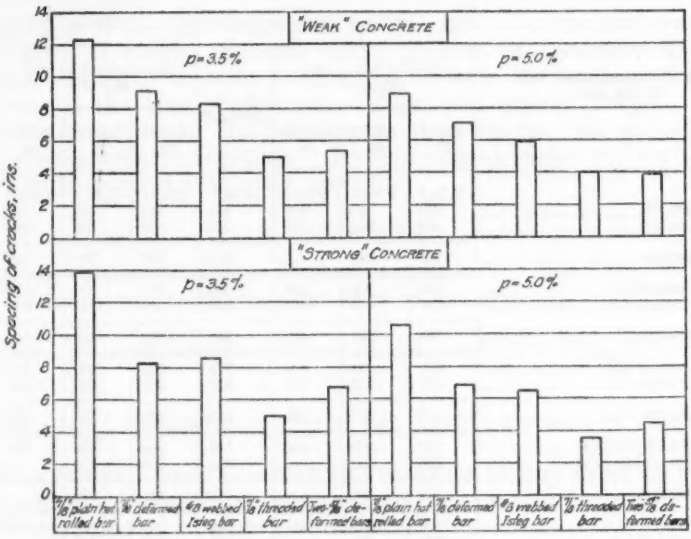

FIGURE 6.—*Spacing of tensile cracks interpolated to correspond to cylinders with reinforcement of 3.5 and 5.0 percent.*

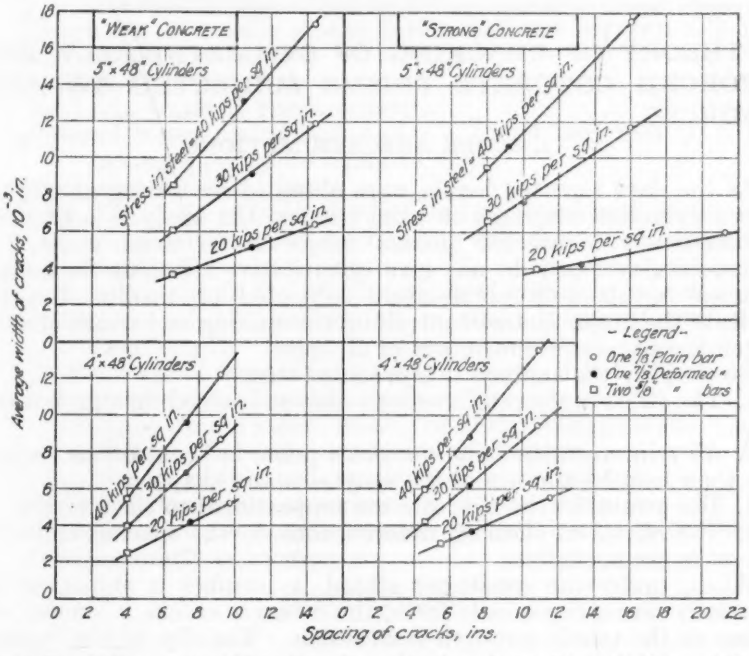

FIGURE 7.—*Relation of widths of cracks to spacing observed in cylinders reinforced with bars of various types.*

TABLE 4.—*Bond strength of test bars*

Bar and direction of pull during test [1]	"Weak" concrete				"Strong" concrete			
	Bond stress at end slip of—			Bond strength	Bond stress at end slip of—			Bond strength
	0.0001 in.	0.0005 in.	0.0010 in.		0.0001 in.	0.0005 in.	0.0010 in.	
	lb/in.²	*lb/in.²*	*lb/in.²*	*lb/in.²*	*lb/in.²*	*lb/in.²*	*lb/in.²*	*lb/in.²*
⅞ in. plain (d)	240	330	360	440	140	190	220	450
⅞ in. plain (o)	210	280	310	370	250	330	380	560
Average	230	300	340	410	200	260	300	510
⅞ in. deformed (d)	190	290	330	810	240	320	370	1,210
⅞ in. deformed (o)	220	410	490	870	210	510	680	1,410
Average	200	350	410	840	220	410	520	1,310
⅝ in. deformed (d)	360	560	600	770	220	280	310	670
⅝ in. deformed (o)	370	670	790	910	380	860	1,040	1,160
Average	370	610	700	840	300	570	680	910
No. 8 webbed Isteg (d)	300	500	530	540	380	490	510	560
No. 8 webbed Isteg (o)	290	350	.....	360	500	670	.....	680
Average	290	430	.....	440	440	580	.....	620
⅞ in. threaded (d)	490	660	770	1,080	640	1,000	1,180	1,740
⅞ in. threaded (o)	660	980	.....	1,380	650	1,600	.....	2,010
Average	570	820	.....	1,230	650	1,300	.....	1,870

[1] Specimens with concrete placed in the direction of pull applied to the bar are designated (d); specimens with concrete placed in the direction opposite to pull applied to the bar are designated (o).

V. THEORY OF CRACKING OF SYMMETRICALLY REINFORCED CONCRETE PRISMS SUBJECTED TO AXIAL FORCES

1. SCOPE AND ASSUMPTIONS

As the data reported herein were obtained by testing axially reinforced cylinders subjected to axial tension, the analysis is limited to symmetrically reinforced prisms subjected to axial stress. The equations developed do not give quantitative relations for nonsymmetrical members or for members subjected to bending, but they indicate the major factors controlling the spacing and width of cracks in reinforced-concrete members of all types.

To simplify the analysis it is assumed that:

1. The stress in the reinforcement does not exceed the "proportional limit."
2. All reinforcement bars in a given prism are continuous throughout their lengths and are of the same size and shape.
3. The strains in the concrete are proportional to the stresses.
4. The effects of shearing deformations on the spacing and width of cracks are negligible.

When, under the conditions stated, a member is subjected to a gradually increasing tensile force, the concrete cracks at one or more places as the tensile strength is exceeded. The slip of the concrete on the reinforcement relieves the stress in portions of the concrete adjacent to cracks, and the tensile stress in the concrete is only that induced by the bond stresses. The distribution of the tensile stress

depends upon the distribution of the bond stress along the reinforcement, which in turn depends upon the amount of slip and the stress in the reinforcement.

Regardless of the distribution of the stresses after the first cracking, the number of cracks increase until, because of excessive slip and reduction of length between cracks, the stress in the concrete does not again exceed the tensile strength. Then, the cracks become wider as the tensile stress in the reinforcement increases, but the spacing of the cracks remains constant. Present consideration will be limited to the conditions existing after cracking.

2. NOTATION

A_c = cross-sectional area of the concrete.
N = number of reinforcement bars in the area A_c.
$A_s = \frac{N\pi D^2}{4}$ (cross-sectional area of the reinforcement in the area A_c).
$D = \sqrt{\frac{4A_s}{N\pi}}$ (diameter of round bar having an area of A_s/N).
C = average tensile stress in the concrete at any cross section.
C_m = tensile strength of the concrete.
E_c = modulus of elasticity of concrete.
E_s = modulus of elasticity of reinforcement.
f_s = tensile stress in reinforcement at a crack.
K_1, K_2 = dimensionless coefficients, the values of which depend upon the distribution of bond stress.
L = spacing of tensile cracks (axial distance between adjacent cracks).
$n = E_s/E_c$.
$p = A_s/A_c$. (ratio of reinforcement).
u = bond stress (calculated as for a round bar, that is, a bar having a perimeter equal to πD).
u_m = maximum bond stress.
$R = u_m/C_m$ (ratio of bond strength to tensile strength of the concrete—an index of the bonding efficiency of the reinforcement).
S = tensile stress in the reinforcement at any cross section.
T = increase in temperature of member (assumed uniformly distributed).
V = shrinkage of concrete per unit of length, if not restrained.
W = average width of tensile cracks in the concrete.
x = distance from a crack, measured along reinforcement.
Z_c = coefficient of thermal expansion of concrete.
Z_s = coefficient of thermal expansion of reinforcement.
$P = N\pi D$ (summation of perimeters of bars in the area A_c).
s = slip per unit of length between concrete and reinforcement.
e = extensibility of concrete.

3. EQUATIONS

(a) GENERAL

At a distance x from a crack $\left(0<x<\frac{L}{2}\right)$ the tensile stress in the con-

crete equals the force transmitted by bond divided by the area of the concrete, that is,

$$C=\frac{P}{A_c}\int_0^x udx=\frac{4p}{D}\int_0^x udx. \tag{1}$$

Similarly, the stress in the reinforcement is given by

$$S=f_s-\frac{P}{A_s}\int_0^x udx=f_s-\frac{4}{D}\int_0^x udx. \tag{2}$$

The tensile stress in the concrete may reach its maximum value only at $x=L/2$, or the maximum value may be approximately constant over a considerable length during the early stages of cracking. However, as cracking continues, the spacing of the cracks becomes smaller until a limiting value of spacing is reached at which the tensile stress does not exceed the tensile strength of the concrete. From eq 1 the maximum stress in the unbroken portion of concrete of length L is

$$C_m=\frac{4p}{D}\int_0^{L/2} udx, \tag{3}$$

from which an estimate of the minimum spacing of cracks, L, may be found if the distribution of the bond stress is known.

The total elongation of the concrete per unit of length for any value of x is the sum of deformations resulting from stress, shrinkage, and change in temperature, that is

$$C/E_c-V+TZ_c. \tag{3a}$$

Similarly, the elongation of the reinforcement is

$$S/E_s+TZ_s. \tag{3b}$$

The slip per unit of length, between the concrete and the reinforcement, is the difference between the elongations per unit of length of the reinforcement and of the concrete, or

$$s=\frac{S-nC}{E_s}+V+T(Z_s-Z_c). \tag{4}$$

The average width of crack is the summation of the slip per unit of length between two adjacent cracks, or

$$W=2\int_0^{L/2} sdx. \tag{5}$$

Equations 3 and 5 may be solved to find the spacing and width of cracks if the form of distribution of the bond stress is known. However, the actual distribution of bond stress cannot be predicted with accuracy. The evidence available [1, 2, 3] indicates that it varies with the amount of slip, the shape or surface roughness of the reinforcement, and the nature of the forces acting on the member. Nevertheless, general solutions indicate the relations of the various factors, and a few particular solutions show the nature of the effect of variations of the distribution of stresses.

To find the minimum spacing of cracks, L, let $u=u_m f\,(x/L)$. Then

$$\int_0^{L/2} udx=u_m\int_0^{L/2} f\left(\frac{x}{L}\right)dx=u_m L\int_0^{1/2} f(X)dX,$$

in which $X=x/L$.

Inserting this in eq 3 and solving for L give

$$L=\frac{K_1C_mD}{u_mp}=\frac{K_1D}{Rp}, \tag{6}$$

in which

$$K_1=\frac{1}{4\int_0^{1/2}f(X)dX}. \tag{7}$$

Substituting from eq 1, 2, 4, and 6 and integrating eq 5 give for the width of cracks, W,

$$W=L\left[V+T(Z_s-Z_c)+\frac{f_s}{E_s}-\frac{K_2C_m}{E_s}\left(\frac{1}{p}+n\right)\right]. \tag{8}$$

Or

$$W=\frac{K_1D}{Rp}\left[V+T(Z_s-Z_c)+\frac{f_s}{E_s}-\frac{K_2C_m}{E_s}\left(\frac{1}{p}+n\right)\right], \tag{8a}$$

in which K_2 is found by the method used to obtain K_1 and is given by

$$K_2=8K_1\int_0^{1/2}dX\int_0^X f(X)dX. \tag{9}$$

(b) EVALUATION OF COEFFICIENTS K_1 AND K_2 FOR ASSUMED DISTRIBUTIONS OF STRESSES

An indication of the effects of variations in the distribution of the bond stress may be obtained by calculating values of K_1 and K_2 for assumed forms of $u=u_mf(x/L)$. Three of these forms are illustrated in figure 8, each one of which may be considered as a rough approximation of a possible distribution of stresses. Calculated values of K_1 and K_2 are as follows:

Assumption	I	II	III
K_1=	1/2	3/4	1.0
K_2=	1/2	5/8	2/3

Although the distribution of stress in case I is physically impossible, it was included in the discussion, since it is often assumed by designers for the sake of simplicity.

(c) CRACKING CAUSED BY SHRINKAGE AND CHANGE IN TEMPERATURE

(1) *Members not restrained.*—For members not restrained by external forces, $f_s=0$, and equation 8a may be written

$$W=\frac{K_1D}{Rp}\left[V+T(Z_s-Z_c)-\frac{K_2C_m}{E_s}\left(\frac{1}{p}+n\right)\right]. \tag{10}$$

For these members the stresses are induced by differential length changes between the concrete and the reinforcement. Before the concrete cracks, the force in the concrete, CA_c, is equal and opposite to that in the reinforcement, SA_s, and the deformations are equal. By equating expressions 3a and 3b and expressing S in terms of C, the tensile stress in the concrete is given by

$$C=\frac{E_sp}{1+pn}[V+T(Z_s-Z_c)]; \tag{11}$$

the concrete will not crack until $C=C_m$, the tensile strength.

(2) *Members fully restrained.*—For members completely restrained to prevent changes in over-all length

$$LT\,Z_s+\frac{2}{E_s}\int_0^{L/2} Sdx=0.$$

Substituting the value of S from eq 2 and solving for f_s, gives for the maximum tensile stress in the reinforcement at a crack:

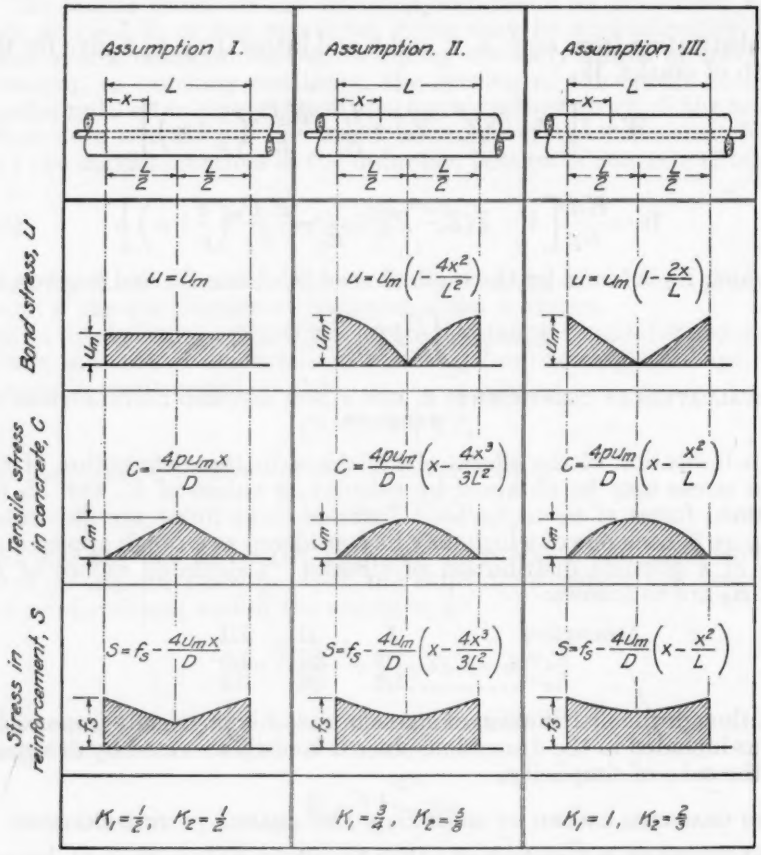

FIGURE 8.—*Assumed distribution of stresses.*

Values of the equations for S, C, and u are plotted for $0<x<L/2$.

$$f_s=\frac{K_2C_m}{p}-E_sTZ_s. \tag{12}$$

Before cracking, the tensile stress in the concrete is

$$C=(V-TZ_c)E_c, \tag{12a}$$

and the concrete cracks when C equals C_m, the tensile strength.

The minimum spacing of the cracks is given by eq 6, and the widths of cracks are obtained by substituting the value of f_s given by eq 12 in eq 8a.

$$W=\frac{K_1 D}{Rp}\left[V-TZ_c-\frac{K_2 C_m n}{E_s}\right]. \quad (13)$$

Obviously, if the reinforcement yields in tension, the width of cracks may become much greater than indicated by eq 13. Hence, if reinforcement is used to control the widths of cracks, the value of f_s given by eq 12 should not exceed the yield strength.

VI. COMMENTS ON THE THEORY

As indicated in the discussion of the test data, the widths of cracks were found to be proportional to the stress above "the stress at zero width of crack." The stress for zero width of crack corresponds to the quantity $K_2 C_m\ [(1/p)+n]$ in eq 8, 8a, and 10 and to $K_2\ C_m\ n$ in eq 13. Under the assumptions, $nC_m=eE_s$ and $C_m\ [(1/p)+n]=C_m/p+eE_s$, in which e is the extensibility of the concrete. It is seen that the properties of the concrete affecting the magnitude of the stress at zero width of crack are the tensile strength and the extensibility, the strength being the more important for all but high values of p, except in eq 13 for members completely restrained, when only the extensibility governs.

Although the values of tensile strength and modulus of elasticity of concrete cannot be predicted accurately, the stress at zero width of crack is much smaller than the other quantities within the brackets of the equations for width of cracks in most practical cases. Hence, a considerable error in estimating their value has a relatively small effect on the estimate of W. Perhaps the largest errors are those in estimates of n, as the strains are not proportional to the stresses, as assumed, and the deformations may be increased greatly by creep or plastic flow under sustained stresses. However, these errors may be minimized by selecting the value of n corresponding to the average stress between $x=0$ and $x=L/2$ and by adjusting n for the effect of creep of the concrete.

Creep in bond (slip under sustained load) decreases the tensile stress in the concrete and increases the width of cracks. The limited information available indicates that the effect of creep in bond is small in comparison with other movements, except when the stresses are large at early ages of concrete and when members reinforced with plain bars are subjected to repeated loading.

In the development of the equations, the effects of shearing deformations in the concrete were disregarded. Because of these deformations, the tensile stress in the concrete is greatest next to the reinforcement, and it decreases with distance from the reinforcement. Accordingly, the tensile resistance of the concrete is less than that indicated by eq 1; in effect this is equivalent to reduction in A_c or an increase in p. The effects of shearing deformations would depend somewhat on the spacing of the cracks and would be greatest when the reinforcement is widely spaced.

The three assumed distributions of bond stress between $x=0$ and $x=L/2$, illustrated in figure 8, are rough approximations of those found experimentally under a variety of conditions [1, 2, 3]. Test data on pull-out specimens indicate that, with a very small slip of the loaded end of the reinforcement, the bond stress is greatest at

that end. For plain bars, the bond stress at the loaded end increases to a maximum value and then decreases slightly, the plane of maximum bond stress moving toward the unloaded end as the slip continues to increase. With an effectively deformed bar, the maximum bond stress occurs at the loaded end and increases with an increase in slip, reaching much higher values than with smooth bars. Aside from these generalizations, the form of distribution of bond stress is not known, and present knowledge is insufficient to indicate the form most applicable to the present problem.

Before the spacing of cracks has reached the minimum value, there are likely to be lengths between cracks in which the bond stress is zero. The conditions during the early development of cracks were not considered in deriving the equations, but, as previously indicated, the form of the equations for the spacing and width of cracks would not be affected.

The equations show that the spacing and width of cracks are inversely proportional to R, the ratio of u_m to C_m. Data showing explicitly how u_m varies with C_m are not available, but there is some evidence indicating that the departure of the ratio R from a constant is not large for a given type of reinforcement bar used in ordinary concretes containing dense aggregate. Therefore, the value of this ratio depends chiefly on those factors that affect the bond strength with a given concrete. The results of bond tests, especially those of Menzel [4] and Robin et al [5], show that, with all other conditions remaining constant, the bond strength is greatly influenced by the orientation and position of the reinforcement in the member. Aside from this, it has been repeatedly demonstrated that, for a given slip, the bond strength is much greater with well designed deformed bars than with plain bars, indicating that R is correspondingly greater with the deformed bars.

The value of u_m of most significance with respect to cracking is the maximum bond stress corresponding to a slip at a crack equal to one-half of the width of the crack. In tests of ordinary pull-out specimens, only the average stresses for various slips are determined, and this varies with the length of embedment of the reinforcement. Another procedure would be preferable for obtaining quantitative values of u_m or R. Nevertheless, it seems likely that existing data on bond provide useful estimates on the relative values of R for various types of reinforcement bars.

Repeated applications of the load causing cracks produce some increase in the widths of cracks. This effect is discussed in another section.

VII. COMPARISON OF TEST DATA WITH THEORY

As previously indicated, the minimum spacing of cracks in the tensile specimens and their width, after the spacing had approached the minimum value, varied approximately as indicated by eq 6 and 8a. In particular, the spacing increased with D/p (see eq 6) and was roughly in reverse order to the bonding effectiveness of the bars as determined by pull-out tests. The widths of cracks were linearly related to L/E_s and to the stress in the reinforcement at a crack; the "stress at zero width of crack" was greater with the "strong" than with

the "weak" concrete and decreased with an increase in the ratio of reinforcement.

The degree of concordance between the data and the theory may be judged by comparing the values of K_1/R and K_2 computed from two distinct sets of experimental data independently determined, viz., the values of the spacing of cracks, and their widths. The values of K_1/R and K_2 are given in table 5, together with the equations used in their evaluation.

TABLE 5.—*Experimental values of dimensionless coefficients K_1/R and K_2.*

Values were computed from the dimensions of the specimens, properties of the materials, the observed values of the minimum spacing of cracks, L, the slope X, and the intercept Y of the straight lines shown in figures 3 and 4, as follows:

Column 2, $\frac{K_1}{R}=\frac{Lp}{D}$, based on spacing of cracks eq 6.

Column 3, $\frac{K_1}{R}=\frac{XE_sp}{D}$, based on the observed relation between width of cracks and the stress in the reinforcement, eq 8a and $W=X(f_s-Y)$.

Column 6, $K_2=\frac{Y}{C_m\left(\frac{1}{p}+n\right)}$, based on the "stresses at zero width of crack," eq 8a and $W=X(f_s-Y)$.

Column 7, $K_2=\frac{XYE_s}{LC_m\left(\frac{1}{p}+n\right)}$, based on the "stresses at zero width of crack" and the slopes of the stress-crack-width graphs, eq 8 and $W=X(f_s-Y)$.

Kind of bar	K_1/R		K_1/R, average	Relative[1] values of K_1/R	K_2		K_2, average
1	2	3	4	5	6	7	8
⅝-in. plain	0.53	0.59	0.56	1.00	0.65	0.71	0.68
⅝-in. deformed	.36	.40	.38	.68	.56	.61	.59
Two ⅝-in. deformed	.34	.37	.36	.64	.46	.51	.48
No. 8 Isteg	.32	.34	.33	.59	.50	.52	.51
⅞-in. threaded	.23	.23	.23	.41	.39	.39	.39

[1] Considering $K_1/R=1$ for the ⅝-in. plain bar.

The two values of K_1/R for each type of bar, one (col. 2) computed from measured values of the spacing and the other (col.3) from the observed relations between the stress in the reinforcement and the width of cracks, were within 6 percent of the average (col. 4). Similarly, the values of K_2 for each type of bar, computed from the observed "stress at zero width of crack" (col. 6) and those computed from the observed slopes of the stress-crack width graphs and the spacing (col. 7), also were within 6 percent of the average (col. 8). Considering the large dispersion of most data obtained in tensile and bond tests of concrete, these results indicate a fair correspondence between the data and the theoretical relation between the spacing and the width of cracks. Some of the other relations indicated by the theory are not so well supported by the experimental data.

The average values of K_1/R with the "strong" concrete was 5½ percent greater than with the "weak" concrete, which is hardly a significant difference. The values for the 5-in. cylinders averaged 15 percent less than for the 4-in. cylinders, indicating that the spacing of cracks decreased somewhat less rapidly than D/p. However, for two types

of bars K_1/R was slightly larger, indicating that the departure from direct proportionality between the spacing and D/p may not be significant.

The relative values of K_1/R given in table 5 are roughly in the same order as the values of the ratios of the tensile strengths of the concretes to the bond strengths in table 4. These data on bond strength are not concordant, in that the bond stresses were in many instances larger with the "weak" than with the "strong" concrete, and the effect of the direction of placing the concrete with respect to the direction of pull was not consistent. Moreover, the different bars were not rated in the same order for the several given values of slip at the free end of the pull-out specimens. The reasons for the discrepancies are not known, but it is clear that the data do not afford a satisfactory means for checking the relations between values of R based on the results of bond tests and those computed from data on the spacing and width of cracks.

According to the analysis, the value of K_2 depends only on the distribution of the bond stress with a given type of bar. The variations of K_2 with the strength of the concrete and with the ratio of reinforcement observed experimentally may be largely the result of chance, as the computed values of K_2 depended on the extrapolated values of "stress at zero width of crack," which showed large dispersions for similar specimens. However, there are other possible causes of the variations, a consideration of which justifies doubt as to their general significance. The average value of K_2 with the 4-in. cylinders was 0.51 and with the 5-in. cylinders was 0.54. This difference may have resulted from a difference in the distribution of bond stresses and from the more pronounced effects of slight eccentricities of loading on the smaller cylinders. But a part of it may have been caused by ignoring the effect of shrinkage of the concrete prior to the loading. If shrinkage occurred before the tests, all of the values of K_2 in table 5 are somewhat lower than the true values. And, making allowance for a shrinkage of less than 0.005 percent would result in equalizing the values of K_2 for the 4-in. and the 5-in. cylinders.

With the "weak" concrete the average value of K_2 was 0.58 and with the "strong" it was 0.48. Again, a small shrinkage of the specimen before testing, ignored in computing the values of K_2 from the data, would cause both values to be too low, but the effect of shrinkage presumably would be greater for the richer "strong" concrete. However, there is another reason for believing that the large difference in the values of K_2 with the two concretes may not be typical of concretes in general. The tensile strength of the "weak" concrete was less and that of the "strong" concrete was more than for typical concretes of the compressive strengths given in table 2. Values from a larger number of tests of gravel-aggregate concretes tested by others indicate a ratio of 270:420 instead of 250:450 for the tensile strengths of concretes having compressive strengths in the proportion 2900:5300 (table 2). The extensibility, e, of the concretes, estimated from measured strains in the reinforced tensile specimens, were 110 and 135 millionths, respectively, for the "weak" and the "strong" concretes. Values of K_2 computed by means of the equations of table 5, after substituting eE_c for C_m, are nearly equal. Therefore, there is not clear evidence that the values of K_2 are importantly affected by changes in the strength of the concrete.

The values of K_2 were consistently less with the deformed and Isteg bars than with the plain bar and were lowest with the threaded bar. The differences in the average values are too large to be attributed to chance, and they seem too large to be simply the result of different forms of distribution of the bond stresses. Possibly slip occurred at an early age as the result of differential volume changes of the concrete and reinforcement, the slip being greater with the plain than with the deformed bars and least with the threaded bar. However, if it were assumed that the concrete slipped freely on the plain bar and did not slip on the threaded bar, a shrinkage of 0.011 percent of the "weak" concrete and 0.016 percent of the "strong" concrete would be required to account fully for the differences in the values of K_2. As the plain bars are known to offer some resistance to slip and as these values for shrinkage are much larger than seem likely, for the type of curing employed, it is evident that shrinkage and slip are not entirely responsible for the differences in the values of K_2. Another possible cause for the values of K_2 being lower with bars having rough surfaces is the effect of the roughness in forming discontinuities in the surface of the concrete in contact with the bars, these resulting in a lower tensile resistance of the concrete and correspondingly lower values for the "stress at zero width of crack." Of the three factors—distribution of bond stress, differential shrinkage and slip, and discontinuities in the concrete surfaces in contact with the reinforcement—which may have caused the values of K_2 to decrease with an increase in the surface roughness of the reinforcement, the last named seems the most important.

In summary, the simple theory did not account fully for the factors controlling the spacing and width of cracks. In particular, the values of K_2 were dependent upon the shape of the reinforcement and the results of conventional pull-out tests did not provide information for making reliable estimates of R and K_2. Although there were other differences between the theory and the data on spacing and width of cracks, these were too small to be positively significant in view of the possible effects of factors ignored when comparing the data with the equations.

VIII. COMPARISON WITH PREVIOUS WORK

Most of the previous investigations of tensile cracking of reinforced concrete dealt with the cracking of flexural members or with the significance of cracks. As these subjects are outside the scope of this paper, the following review cites only the investigations giving information on the factors governing the spacing and width of cracks.

In tests of members subjected to a uniform bending moment over a considerable length, Considĕre [6] found that, when the ratio of reinforcement was the same, the spacing of cracks increased with the diameter of the reinforcement. Similar tests by Bach and Graf [7] confirmed the findings of Considère and showed that the width of cracks was less when the surface of the reinforcement was rough than when it was smooth. For a range of loading between the design load and that causing yielding of the reinforcement, the widths of cracks were roughly proportional to the spacings. These investigators, as well as Berry [8], Slater [9, 10, p. 421], and Probst [11], found that, under the usual conditions of service, the number of cracks is

increased slightly and the width considerably by repeated loading. The increases were greatest for the first few repetitions, after which the number and width of cracks changed by only small amounts. More recent investigations [12, p. 186] indicate that the increase in width of cracks under repeated loads is much smaller with deformed bars than with plain bars.

Taylor and Thompson [13, p. 565–69] report an analysis of the stresses in symmetrically reinforced concrete members caused by shrinkage and change in temperature and showed that the spacing of cracks is proportional to D/p. They pointed out that reinforcement which provides a mechanical bond is more effective than smooth bars in distributing and controlling the width of cracks.

Slater [10, p. 461] measured the widths of cracks in the webs of heavily reinforced beams subjected to high shearing stresses. The widths were approximately proportional to the increase of load beyond that causing the cracking. The rate of increase of width with increasing load was substantially independent of the strength of the concrete, but was roughly proportional to the width of the web (or to $1/p$). The extrapolated value for the stress at zero width of crack was approximately proportional to a quantity closely similar to $C_m[(1/p)+n]$, expressed in terms of the compressive strength of the concrete and the width of the web.

Kuznetsov [14] measured spacing and width of cracks in centrally reinforced cylinders in tension and also presented a theoretical analysis of the distribution of stresses in the test specimens. The width and spacing of cracks decreased as the bonded surface of steel and the percentage of reinforcement increased, and repeated application of load caused considerable additional widening of cracks. Equations for distribution of bond stress and the width of cracks were obtained by the author. The equations were derived by consideration of equilibrium of a centrally loaded reinforced cylinder and the basic assumption that the bond stress was proportional to the quantity $(f_s/E_s)-(C/E_c)$.

A theoretical analysis of stresses in a straight, symmetrically reinforced prism produced by shrinkage and change in temperature was reported by Vetter [15]. Equations, based upon a constant bond stress along the reinforcement, were given for the spacing of cracks and the stresses in the concrete and reinforcement. Vetter's equation for the minimum spacing of cracks corresponds to eq 6 with $K_1=1/2$. Other equations are given for calculating the minimum amount of reinforcement to avoid overstressing, for determining the maximum volume change before overstressing and for estimating the spacing of cracks during the early stages of cracking.

In a discussion of Vetter's paper [15, p. 1070] Lester L. Meyer gave data on the spacing and width of cracks in 11 reinforced-concrete slabs tested in tension. The reinforcement in the slabs ranged from 0.25 to 1.50 percent. Sufficient information on the conditions is not given for an estimate of the effects of volume changes on the measured widths of the cracks, and the spacings were somewhat erratic. However, the median value of K_1/R, computed from the data on the minimum spacing, is 0.37, the same as the average value for the deformed bars used in this investigation.

Thomas [16] reported on an investigation of cracking caused both by volume change and strain, the value of prestressing as a preventive and the practical significance of cracks. Equations were given for estimating the stresses caused by shrinkage, taking into account the effects of creep and the degree of restraint. Data and discussion indicate that resistance to cracking of completely restrained members was influenced by the kind of aggregate and is greater with slow hardening than with rapid hardening cement. The resistance to shrinkage cracking was not affected appreciably by variations in the amounts of cement or mixing water in the concrete. Equations for the spacing and width of cracks were based upon a parabolic distribution of bond stress (assumption II of this paper). Data obtained by testing beams were in good qualitative agreement with the equations. Observations showed that cracks tended to close upon releasing loads, but that the resistance to slip delayed this movement until the loads were considerably reduced. Under sustained loads, the widths of cracks in the beams increased about 50 percent, reaching constant values in a few weeks.

Several authors of papers published in the Preliminary Publication of the Second Congress of the International Association for Bridge and Structural Engineering (1936) discussed the significance of cracking, and some of them (other than Thomas) gave data on the factors affecting the spacing and width of cracks. Bornemann (p. 185, et seq.) reviewed data indicating that, with smooth bars as reinforcement, high stresses and repeated loading breaks down resistance to slipping, resulting in an increase in width but not in number of cracks. He states that, when a crack forms, the dynamic effect of the sudden release of tension in the concrete increases the initial width of the crack, this effect being most pronounced with low ratios of reinforcement and concrete of high tensile strength. He concludes that widths of cracks may be minimized by the use of a slow hardening concrete with small shrinkage and slow drying and of small bars with rough surfaces. Colonnetti (p. 191) proves by a theoretical analysis that it is preferable to use a large number of small bars than a smaller number of large ones. Saliger (p. 293) discussed the mechanism of the cracking of reinforced-concrete members, especially beams, gave data on the stress in the reinforcement when the first crack appeared in beams and developed equations for the spacing of cracks based on assumption III of this paper. The advantage of using a large number of small bars with rough surfaces was stressed.

In summary, the previous investigations reviewed give but little quantitative data on the spacing and width of cracks, but the information available indicates that the widths of cracks are roughly proportional to D/p, the rate of increase of width with increase of stress is independent of the strength of the concrete and the stress at zero width of crack is roughly proportional to the strength of the concrete. Reinforcement which provides a mechanical bond not only is more effective than smooth bars in controlling the initial widths of cracks, but also in minimizing the enlargement caused by sustained or repeated loads. The indications of the test data and of the analysis given in this paper are in agreement with the findings in earlier investigations as to the factors controlling the spacing and width of cracks.

IX. PRACTICAL APPLICATIONS

Ordinarily, when it is desired to estimate the probable spacing and width of cracks in reinforced concrete, precise information is not available on the properties of the concrete and the other factors controlling cracking. Consequently, refinements in the equations used in making the estimates are not warranted, and it is convenient to reduce to a minimum the number of quantities to which values must be assigned before numerical solutions are obtained. According to the data of table 5 (col. 4), eq 6, giving the minimum spacing of cracks, may be simplified to read

$$L=0.6D/p \tag{14a}$$

for the plain bar, and

$$L=0.4D/p \tag{14b}$$

for the deformed bars.

Available information on the tensile properties of concretes of ordinary compositions indicates that the value of nC_m from eq 8a, et seq., depends in part on the rate of stressing the concrete and that, except for concrete subjected to high stress at an unusually early age or to unusual storage conditions, the value ranges between 3,000 and 5,000 lb/in.^{2}, being near the lower value in conventional laboratory load tests and near the upper value when the stresses are developed slowly. In most practical cases, nC_m, is not a large part of the total magnitude of the quantity within the brackets of an equation for the width of cracks, and a value of 4,000 lb/in.^{2} for nC_m may be assigned tentatively Using this approximation, eq 8a for the width of cracks in symmetrically reinforced members subjected to tensile forces may be modified to read

$$W=\frac{K_1}{R}\frac{D}{E_sp}\left[VE_s+T(Z_s-Z_c)E_s+f_s-K_2\left(\frac{C_m}{p}+4{,}000\right)\right] \tag{15}$$

By setting $f_s=0$, eq 15 applies to nonrestrained members subjected to shrinkage and change in temperature.

For members fully restrained

$$W=\frac{K_1}{R}\frac{D}{E_sp}[VE_s-TZ_cE_s-4{,}000K_2]. \tag{16}$$

The amount of reinforcement needed to prevent stressing the reinforcement beyond the yield point is, from eq 12,

$$p>\frac{K_2C_m}{Y+E_sTZ_s}, \tag{17}$$

in which Y is the yield point of the reinforcement.

The approximate values of the coefficients indicated by the data of table 5 are $K_1/R=0.6$ and $K_2=2/3$ for the plain bar, and $K_1/R=0.4$ and $K_2=1/2$ for the deformed bars.

When the serviceability of a structure is likely to depend importantly upon the width of the tensile cracks, it is obviously desirable to make the fullest possible use of existing knowledge on methods of minimizing the effects of shrinkage of concrete. The methods of controlling cracking, such as limiting the allowable tensile stress to a value less than that based on consideration of strength, are well known

and are commonly employed, but the choices of materials and design stresses usually are governed by other factors, and, to attain the greatest economy in the use of reinforcement, it is essential that design stresses be as large as are deemed safe. The advantage of using bars of the smallest feasible sizes to give low values of D/p also is well known, but limitations of space often prevent the placing of large number of small bars. Then, the use of reinforcement providing a low value of K_1/R is especially advantageous.

Results of other bond tests [17, 18, 19] indicate that the particular type of deformed bars used in these tests afford higher bond strengths than most of the present-day commercial deformed bars. It would be expected, therefore, that the value of K_1/R for most reinforcement bars would have exceeded 0.4, and for some approached 0.6, the value found for the plain bar. Moreover, investigations [17, 18, 19] indicate that K_1/R for some experimental deformed bars probably is less than 0.2, the value found for the threaded bar. As the enlargement of cracks under prolonged or repeated loading has been found to be greater with plain than with deformed bars, the actual practical advantage of a well designed deformed bar probably is greater than indicated by these tests. The development and use of a type of reinforcement bar that would assure a low value of K_1/R offers promise of more reliable bond and anchorage of reinforcement, better control of the width of cracks and more economical use of steel reinforcement. The recommendations of Abrams [20] and Menzel [19] appear to be satisfactory guides for the design of such a bar.

X. SUMMARY OF RESULTS

1. Widths of tensile cracks interpolated to correspond to specimens with equal percentages of reinforcement were least for specimens reinforced with pairs of ⅝-in. deformed bars or with a ⅞-in. threaded bar. The relative values of the widths of cracks at a stress of 30,000 lb/in.^{2}, representing two percentages of reinforcement and concretes of two strengths, are given in the following table.

Type of bar	*Ratio of width of cracks to that observed for ⅞-in plain hot-rolled bar*
⅞-in. plain hot-rolled	1.00
⅞-in. deformed	0.72
No. 8 webbed Isteg	.75
Two ⅝-in. deformed	.48
⅞-in. threaded	.46

2. For the width of crack observed in specimens reinforced with plain hot-rolled bars carrying a stress of 20,000 lb/in.^{2}, the corresponding stresses for the other bars were, on the average, 24,000 lb/in.^{2} with the Isteg bars, 25,000 lb/in.^{2} with the ⅞-in. deformed bars, and 35,000 lb/in.^{2} with the threaded and the ⅝-in. deformed bars.

3. There was no significant difference between the widths of cracks for a given stress and a given type of bar, as observed in specimens of "weak" and "strong" concrete.

4. The widths of cracks observed in cylinders of the same diameter, and for different bars stressed to the same extent, varied linearly with the spacing of cracks observed for the different bars. This observa-

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tion is true only for reinforcement bars having nearly the same modulus of elasticity.

5. The test data and the theoretical equations were in good agreement with respect to the effects of the principal factors controlling the spacing and width of cracks. The values of the coefficient which determine the "stress at zero width of crack" were markedly affected by changes in the shape of the reinforcement bar.

6. The width of cracks in symmetrically reinforced-concrete members subjected to axial tension and to the effects of shrinkage of concrete and change in temperature may be minimized by:

(a) Using concrete of low shrinkage properties.

(b) Limiting tensile stresses in the reinforcement to low values.

(c) Reinforcing the concrete with the largest number of bars of the smallest sizes compatible with other requirements.

(d) Using deformed bars having projecting lugs that afford resistance against slipping without causing splitting of the concrete and that are spaced to provide the minimum of bearing area necessary to develop the desired bond strength.

XI. REFERENCES

[1] W. H. Glanville, Bond Resistance, Technical Paper No. 10, Building Research Board, Great Britain (1930).

[1a] L. Schuman and John Tucker, Jr., *Tensile and other properties of concretes made with various types of cement.* J. Research NBS **31.** (Publication pending.)

[2] D. Watstein, *Bond stress in concrete pull-out specimens.* J. Am. Concrete Inst. **38**, 37 (1941).

[3] H. J. Gilkey, S. J. Chamberlin, and R. W. Beal, Bond Between Concrete and Steel, Iowa Eng. Exp. Sta. Bul. 147 (1940).

[4] C. A. Menzel, *Some factors influencing results of pull-out bond tests,* Proc. Am. Concrete Inst. **35,** 517 (1939).

[5] R. C. Robin, P. E. Olsen and R. F. Kinnane, *Bond strength of reinforcing bars embedded horizontally in concrete,* Trans. Inst. Engrs. (Australia) **14**, 201 (Sept. 1942).

[6] A. Considère, Handbuch für Eisenbetonbau, 3d ed., p. 104 (1921).

[7] C. Bach and O. Graf, Handbuch für Eisenbetonbau, 3d ed., p. 105 (1921).

[8] H. C. Berry, *Some tests of reinforced concrete beams under oft-repeated loading,* Am. Soc. Testing Materials **8,** 454 (1908).

[9] W. A. Slater, G. A. Smith, and H. P. Mueller, *Effect of repeated reversals of stress on double-reinforced concrete beams,* Tech. Pap. BS **14** (1921) T182.

[10] W. A. Slater, *Shear tests of reinforced concrete beams,* Tech. Pap. BS **20** (1926) T314.

[11] E. Probst, *The influence of rapidly alternating loading on concrete and reinforced concrete,* Struc. Engr. **9,** 410 (1931).

[12] E. Bornemann, Tensile strength and formation of cracks in concrete, Prelim. Pub. Second Cong. Int. Assn. for Bridge and Struc. Eng. (1936).

[13] Taylor and Thompson, Concrete, Plain and Reinforced, 3d ed. (1916).

[14] A. N. Kuznetsov, *Formation of cracks in centrally loaded reinforced concrete specimens,* Stroitel'naya Promyshlennost', U. S. S. R., **18,** 42 (July 1940).

[15] C. P. Vetter, *Stresses in reinforced concrete due to volume changes,* Trans. Am. Soc. Civil Engrs. **98,** 1039 (1933).

[16] F. G. Thomas, *Cracking in reinforced concrete,* The Struc. Engr. **15,** 298 (1936); and Prelim. Pub. Second Cong. Int. Assn. for Bridge and Struc. Eng. p. 223 (1936).

[17] C. J. Posey, Tests of Anchorages for Reinforcing bars, Bul. 3, University of Iowa Studies in Engineering (1933).

[18] G. R. Wernisch, *Bond studies of different types of reinforcing bars,* Proc. Am. Concrete Inst. **34,** 145 (1938).

[19] C. A. Menzel, A Proposed Standard Deformed Bar for Reinforcing Concrete, Proc. 17th Semiannual Meeting Concrete Reinforcing Steel Inst. (1941).

[20] D. A. Abrams, Tests of Bond Between Concrete and Steel, Bul. 71, Univ. of Ill. Eng. Exp. Sta. (1913), p. 212, par. 21.

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RESEARCH PAPER RP1546

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AUTOGRAPHIC LOAD-ELONGATION APPARATUS FOR FIBERS

By Arnold M. Sookne and Henry A. Rutherford [1]

ABSTRACT

An autographic load-elongation apparatus for testing single fibers is described. The apparatus is adapted to making a continuous load-elongation record at constant rate of elongation and to making a point by point record at constant rate of loading. It is also useful for obtaining relaxation curves for single fibers. It combines the principles of a hand-operated machine developed in this laboratory and an automatic electronic balance developed by Muller and Garman [5].[2] Sensitive automatic operation is attained by means of photoelectric controls, and autographic recording in rectangular coordinates is provided. Examples are given of the performance of the apparatus.

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I. INTRODUCTION

In studies of the mechanical properties of textile materials, it has been found useful to investigate the properties of the individual fibers, since complications introduced by yarn structure and weave are thereby eliminated. There have been numerous types of apparatus designed to study the load-elongation properties of single fibers, the descriptions of which are given elsewhere [1, 2, 3]. Some of these machines are very sensitive, and have found wide application in studies of fiber properties. None of them, however, combines autographic operation with sufficient sensitivity for the investigation of weak fibers and sufficient magnification for the investigation of relatively inextensible fibers.

In previous work at the Bureau, a modified chemical balance has been used to obtain load-elongation curves of single fibers [4]. The procedure used with this apparatus was to attach the fiber (mounted on glass hooks) to the left balance beam and to a platform which could be raised or lowered by a rack and pinion. Increments of load were added to the right balance pan, the platform was lowered by

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.
[2] Figures in brackets indicate the literature references at the end of this paper.

means of hand-operated gearing to return the balance pointer to zero, and the elongation was obtained by measuring the displacement of the platform. The test procedure is described in detail elsewhere [4]. This apparatus provides sufficient sensitivity for investigation of weak fibers, but its operation is tedious and slow, and does not allow continuous stretching of the fiber. The basic suitability of the balance principle has been demonstrated, however, and it therefore seemed desirable to adapt a balance apparatus to automatic and autographic operation. The sensitive and stable automatic electronic balance of Muller and Garman [5] provides the means for accomplishing this.

The basis of the present apparatus is a magnetically damped analytical balance equipped with a Chainomatic column. The method of obtaining a load-elongation curve is similar to that described above, but in contrast with the earlier apparatus, the present machine automatically either elongates or loads a fiber at a constant rate. This arrangement combines the high sensitivity of the analytical balance with autographic recording. Constant rate of elongation is obtained by lowering at a constant speed the platform to which the fiber is attached; constant rate of loading is obtained by lowering at a constant rate the end of the chain which is attached to the Chainomatic column. The balance pointer is continuously and automatically maintained at the zero point within close limits by photoelectric controls. For constant rate of elongation the load is recorded continuously as a function of the elongation, but for constant rate of loading the elongation is recorded only at intervals. The recording system could, however, be modified to produce a continuous load-elongation curve for constant rate of loading.

II. CONSTRUCTION

1. GENERAL AND MECHANICAL DESCRIPTION

A general view of the apparatus is given in figure 1. The recording drum (kymograph drum), which is normally mounted on the vertical shaft in front of the balance, has been omitted from this photograph in order to give an unobstructed view of the balance. The kymograph protrudes through a hole in the table top in front of the balance. The box on top of the balance houses the light source for the photoelectric control. The control chassis is at the left of the balance. The motors and gear reducers are mounted on a shelf about 6 in. below the table top, and the power-supply chassis on a shelf at the lower left side of the table, out of the way of the operator. A schematic diagram of the arrangement of the mechanical and optical parts is given in figure 2, from which the recording system has been omitted.

The fiber is elongated by lowering the platform, H, the extent of the elongation being indicated by the dial gage, J, (range 2 in.), which is rigidly attached to the platform by the arm, K. The platform can be controlled manually by means of the rack, L, and pinion, M. The shaft to which the rack is attached is hollowed and split for about 2 in. at its lower end to receive the upper end of the threaded shaft, O. The two shafts can be easily attached by means of the friction clamp, N, and the platform can then be controlled by means of a mechanical drive. Power is transmitted from a constant-speed motor (not shown

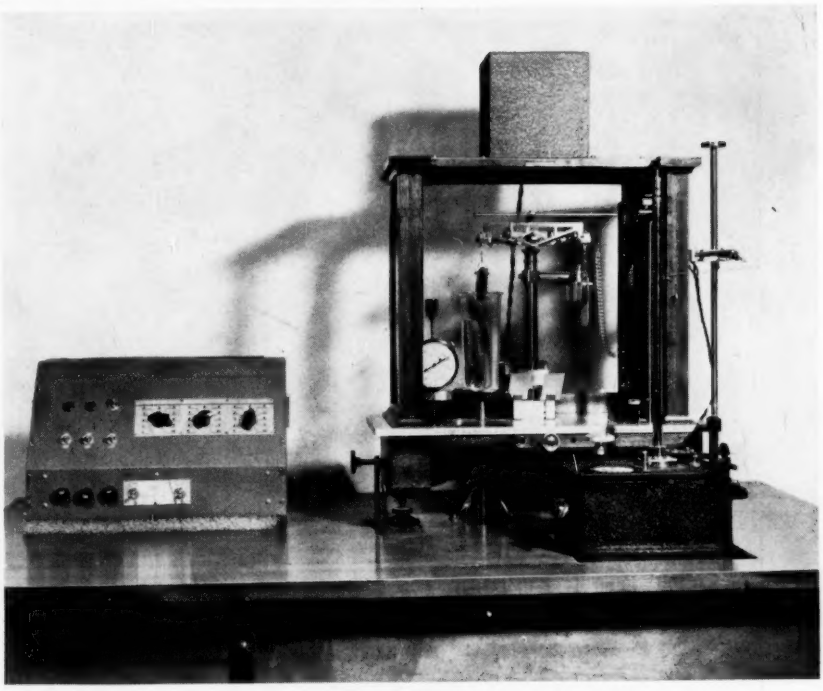

FIGURE 1.—*General view of the autographic load-elongation apparatus.*
The recording drum has been omitted.

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in fig. 2) by means of a gear-box and chain-and-sprocket combination to the sprocket, *R*, the worm, *P*, and the tapped worm-gear, *Q*, which raises or lowers the threaded shaft, *O*, which is provided with a key to prevent rotation.

The load is applied by means of the chain or chains, *E*. Power is transmitted through a gear-box and chain-and-sprocket drive to the

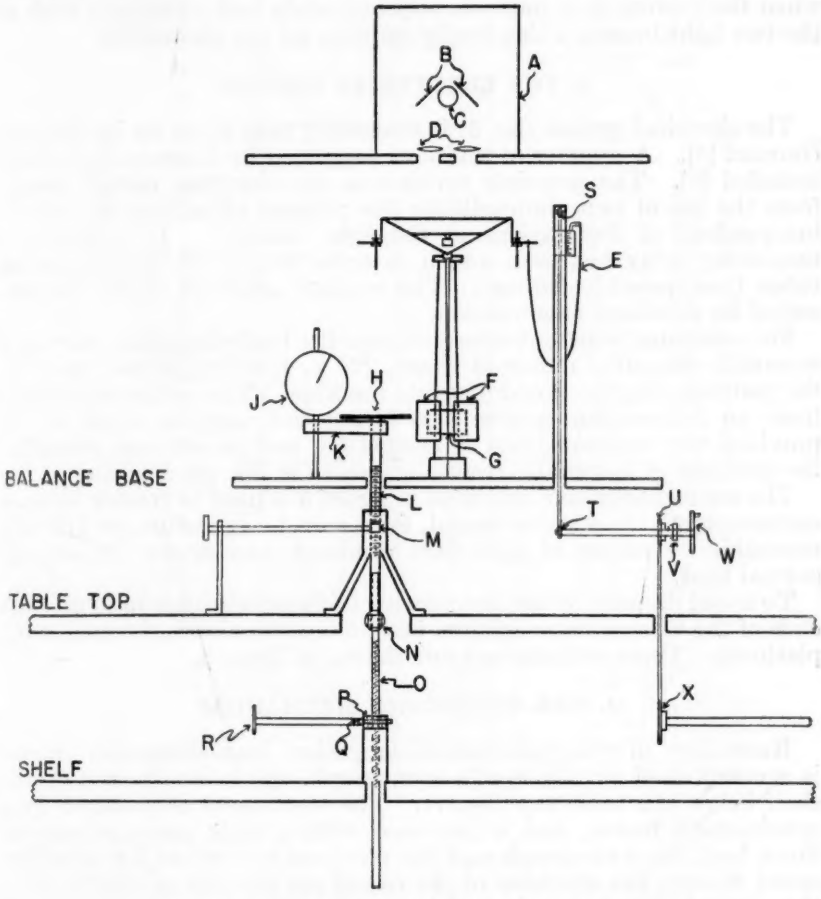


FIGURE 2.—*Schematic diagram of the apparatus.*

A, housing for light source; *B* and *F*, mirrors; *C*, light source; *D*, condensing lenses; *E*, chain; *G*, target; *H*, platform; *J*, dial gage; *K*, connecting arm; *L*, rack; *M*, pinion; *N*, friction clamp; *O*, threaded shaft; *P*, worm; *Q*, worm gear; *R*, *S*, *T*, *U*, and *X*, sprockets; *V*, clutch; and *W*, wheel for hand operation of chain.

sprockets, *X* and *U*. The vernier of the Chainomatic column, to which the chain is fixed, is driven by a sprocket chain and the sprockets, *S* and *T*. A simple clutch, *V*, is provided adjacent to the sprocket, *U*, so that the chain may be controlled manually by means of the wheel, *W*, or by the motor drive.

2. THE OPTICAL SYSTEM

The arrangement of the optical parts is shown in figure 2. The two light beams originate in the 6 to 8 v, 21 candlepower lamp, *C*, housed

in the box, *A*, which is provided with baffles. The beams are reflected downward by the metal mirrors, *B*, through the condensing lenses, *D*. The mirrors, *F*, placed symmetrically in front of the target, *G*, send the beams past the target and to the photocells. (The photocells have been omitted from fig. 2 in the interests of clarity, but they can be seen behind the balance in fig. 1.) Automatic control of the position of the balance pointer is obtained with the help of the target, which, when the system is in balance, approximately half-interrupts each of the two light beams, which finally impinge on the photocells.

3. THE ELECTRICAL SYSTEM

The electrical system (fig. 3) is essentially that given by Muller and Garman [5]. A number of revisions suggested by Garman have been included [6]. The principle revision in the electrical circuit results from the use of two photocells for the purpose of making the circuit independent of fluctuations in the light source. In addition, a time-delay relay has been added in order to protect the thyratron tubes from possible damage. The original article [5] should be consulted for details of construction.

For obtaining constant-rate-of-elongation load-elongation curves, a reversible induction motor (3 phase, 220 v, 1/15 hp) is used to lower the platform (*H*, fig. 2) and elongate the fiber. This motor is powered from an independent source and is not indicated in figure 3. It provides very constant rate of elongation, and in addition simplifies the problem of automatic recording, which is discussed below.

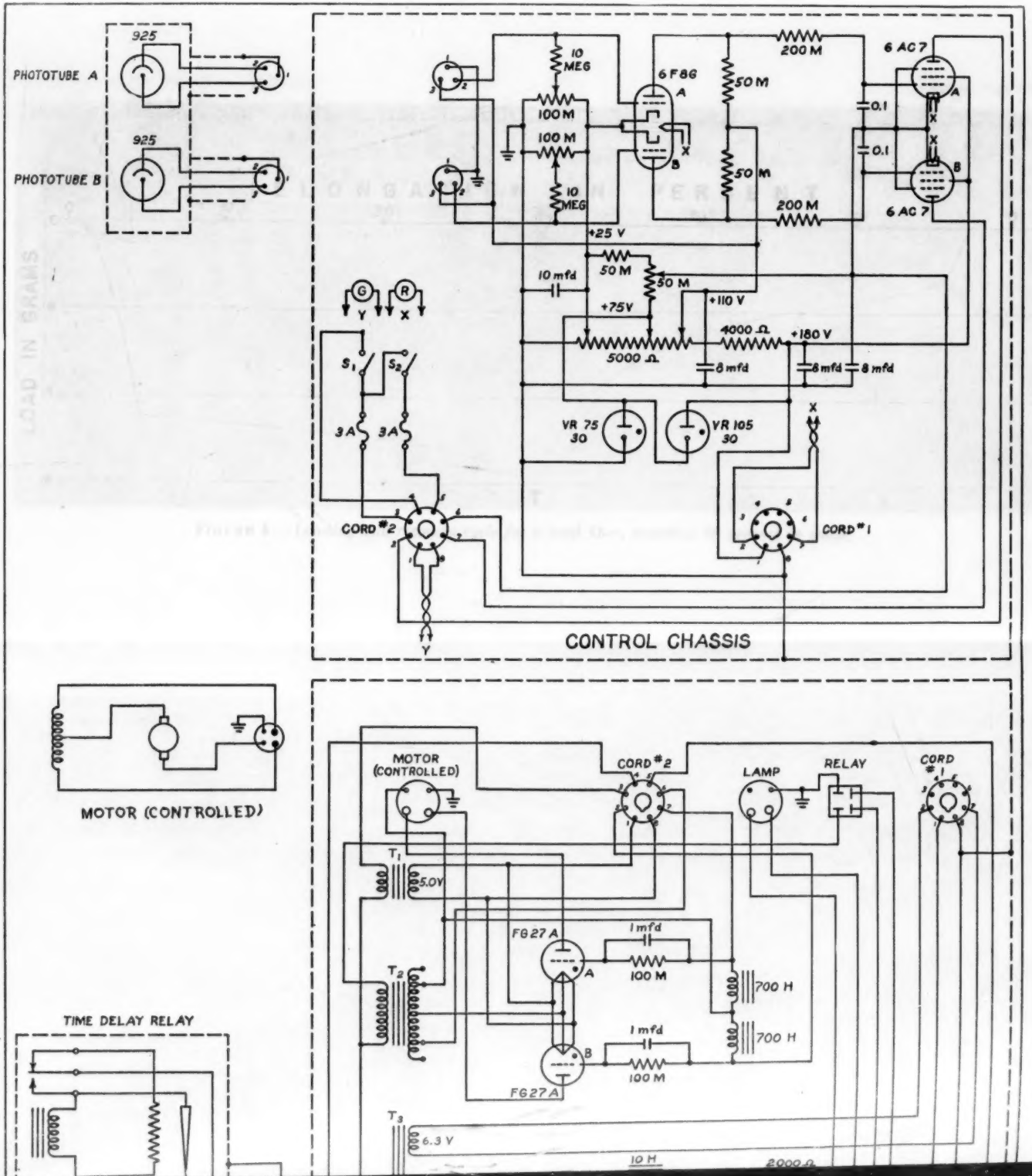
The controlled motor indicated in figure 3 is used to restore balance continuously. It is series wound, for a-c or d-c operation on 115 v, is reversible by means of split field windings, and draws 0.8 amp at normal load.

To avoid damage to the instrument, limit switches are used on both ends of the Chainomatic column, and at the lower limit of travel of the platform. These switches are not shown in figure 3.

4. THE RECORDING MECHANISM

Recording of constant-rate-of-elongation load-elongation curves is accomplished by means of a kymograph, which is mounted on the shelf below the table top (fig. 1). The instrument is powered by a synchronous motor, and is provided with a wide range of speeds. Since both the kymograph and the platform are driven by constant-speed motors, the abscissas of the record are directly proportional to the elongation. It has been found convenient to mark the axis of abscissas at regular intervals of elongation (0.003 in. or 0.03 in.) by means of signal magnets, or time markers. These are motivated by switches controlled by cams set on a rotating shaft of the platform drive. Rates of elongation from 0.05 to 0.2 in. per minute have been used, but a wider range of rates is easily available.

The load at any elongation is recorded by means of a swivel-mounted writing pen (this is the lower pen in fig. 1) attached to the vernier of the Chainomatic column. The apparatus thus provides a directly recorded load-elongation curve. The ordinates are directly proportional to load, the factor of proportionality depending upon the chains used. Chains (or combinations of chains) for which 1 in. of record corresponds to 2, 4, and 6 g have been used.


PHOTOTUBE A
925
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200 M
6 AC 7
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B
6 AC 7
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+25 V
10 mfd
50 M
30 M
+110 V
+75V
4000 Ω
+180 V
5000 Ω
8 mfd
8 mfd
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S1
S2
3A
3A
VR 75
30
VR 105
30
X
CORD #2
CORD #1
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CONTROL CHASSIS
MOTOR (CONTROLLED)
MOTOR (CONTROLLED)
CORD #2
LAMP
RELAY
CORD #1
T1
5.0V
FG27A
A
1 mfd
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TIME DELAY RELAY

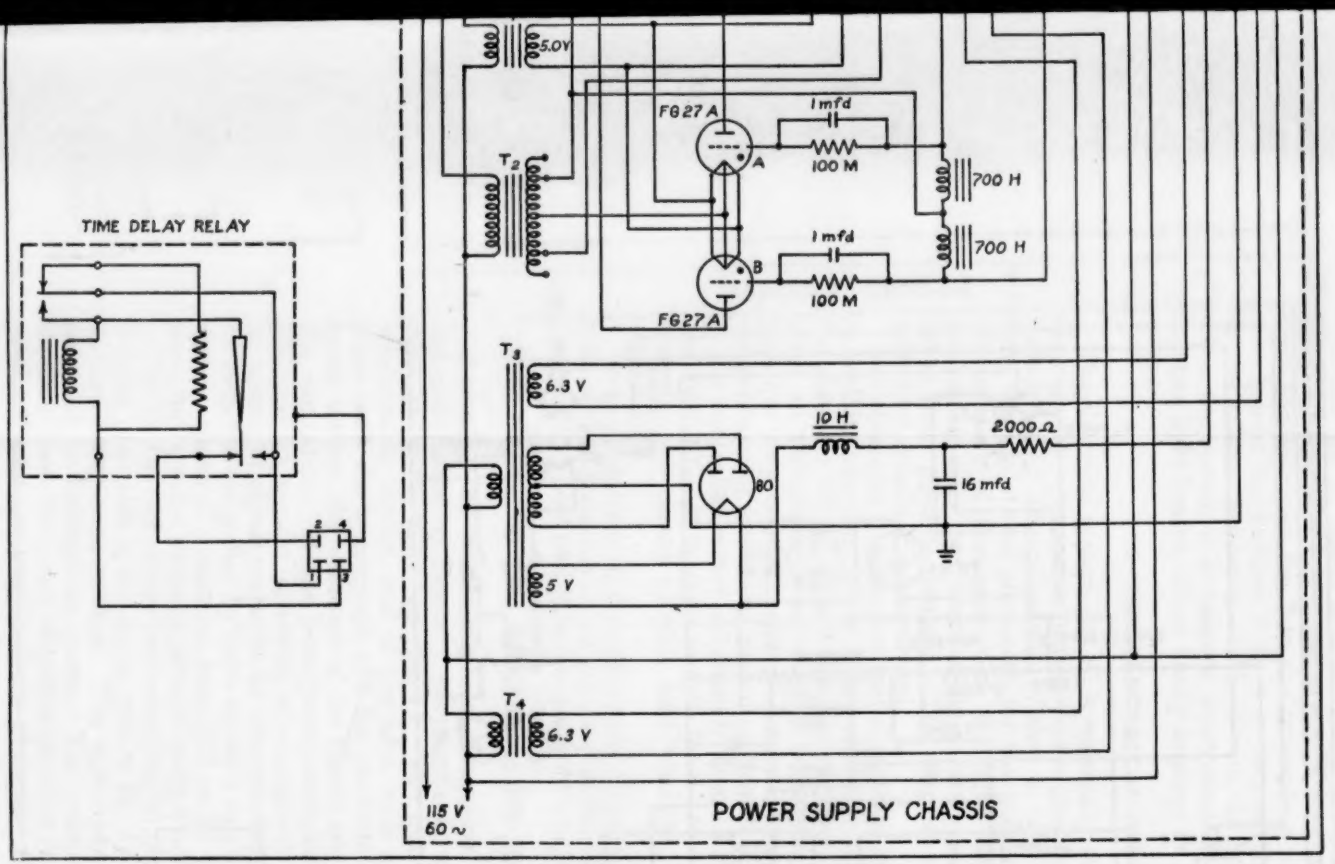

FIGURE 3.—*Diagram of the electrical circuit.*

The symbol *M* denotes: 1,000 ohms.
T_1=Filament transformer, 5 v center tap, 13-amp secondary.
T_2=Power transformer rewound so that secondary gives 175 or 180 v a-c, 250 ma on either side of tap.
T_3=Power transformer, 385-0-385 v, 70 ma, 5 v, 2 amp, and 6.3 v, 2.5 amp center tap secondaries.
T_4=Filament transformer, 6.3 v center tap, 6-amp secondary.
Time delay relay: Delay 1 minute, immediate recycling, coil 110 v a-c, 60 cycles, contacts 110 v a-c amp.
Ckokes: 700 h, 0.5 ma, 6,150 ohms.

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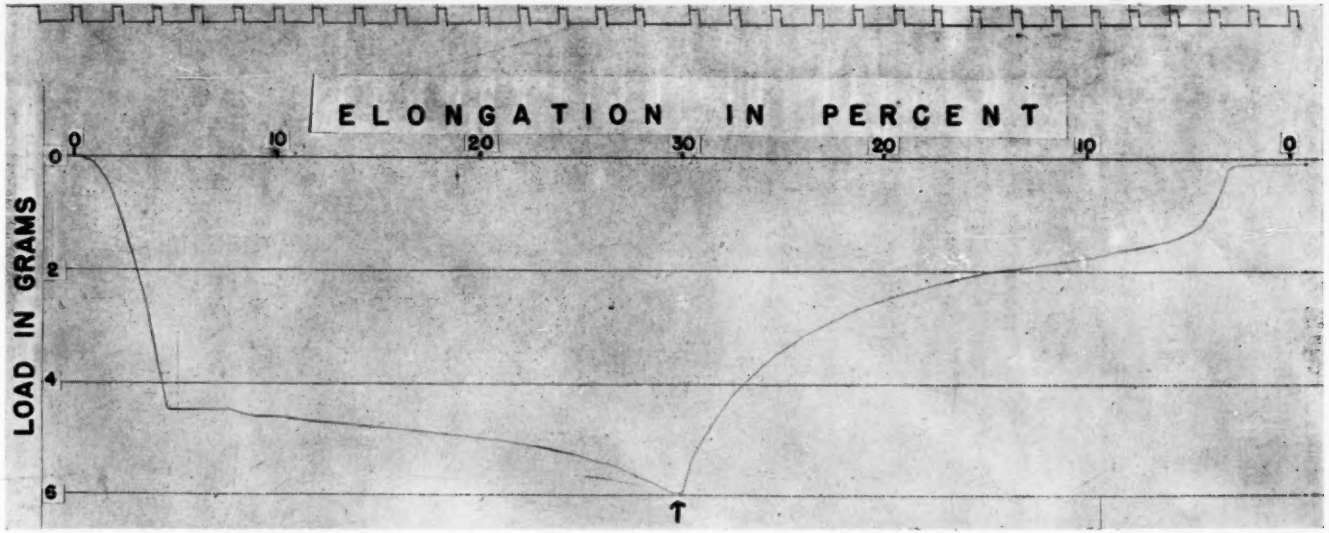

FIGURE 4.—*Loading and recovery cycle for a wool fiber, stretched 30 percent in water.*

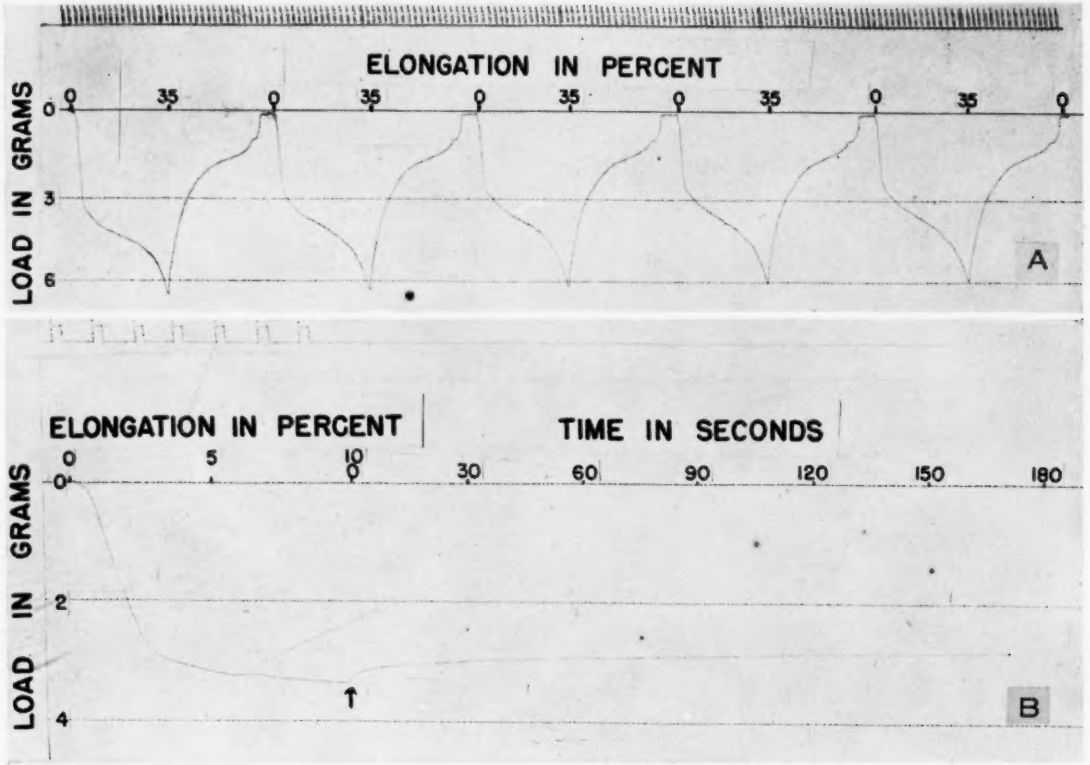

FIGURE 6.—*Load-elongation and relaxation curves for single wool fibers.*

A, Successive loading and recovery cycles for a wool fiber, stretched 35 percent in water five times; *B*, relaxation curve for a single wool fiber. The fiber was stretched to 10-percent elongation in the wet state, and then allowed to relax.

III. OPERATION AND EXAMPLES

At the start of a load-elongation experiment, a mounted fiber, calibrated with respect to length and average cross section, is hung from the left balance beam, and the balance pointer is brought to the zero point by manual adjustment of the chain or a rider on the balance beam. A flask with a glass hook sealed to the bottom is then set on the platform (*H*, fig. 2) if the fiber is to be elongated wet; a weight with a hook attached is used if the experiment is to be conducted in a conditioned atmosphere. The friction clamp, *N*, is then loosened, and the platform is adjusted manually with the rack and pinion so that the glass hook on the lower end of the fiber engages the hook of the flask or weight. The platform is lowered until the balance pointer is just displaced. The dial-gage reading at this point is the initial value (zero elongation). The friction clamp, *N*, is tightened with the balance pointer at zero, the controls are turned on, and the motor which lowers the platform is started. The machine thereafter records the load-elongation curve for the fiber automatically. Hysteresis curves can be obtained by reversing the motor which lowers the platform at any given elongation. The dial gage serves to indicate when a required elongation has been reached during an experiment. At the end of the experiment, lines corresponding to any given values of load or stress may be marked on the drum by lowering the chain with its writing pen, and rotating the kymograph drum by hand. The abscissa values may be easily obtained from the signal-magnet tracings.

Successful automatic operation depends on the proper adjustment of the speed of the platform, the motion of the chain, the size of the chain used, and the sensitivity of the controls. In particular, the chain must be capable of moving rapidly enough to take care of the most rapid changes of load (usually in the Hooke's law portion of the curve). The chain should be light enough, however, so that the scale of the ordinates is not unduly compressed. The scale of the abscissas may be easily adjusted by changing the speed of the kymograph drum.

Automatically recorded constant-rate-of-loading load-elongation curves can be obtained by running the chain side at a constant speed, and using a controlled motor on the platform side. Since the kymograph drum is driven at a constant rate by a synchronous motor, and since the platform is driven by the controlled motor, which does not run at a uniform rate, the elongation is not proportional to the abscissas lengths under these conditions. The recording system could be modified to give the conventional type of record for both constant-rate-of-loading and constant-rate-of-elongation experiments. This could be accomplished by using the motor which lowers the platform to rotate the kymograph drum as well. This change would, however, involve difficulties arising from backlash in the long gear train, which gives the kymograph its desirable range of speeds. In addition, the apparatus would not then be suitable for relaxation studies.

The factor which limits the accuracy of the results appears to be the uniformity of the chains used to load the fiber. For small loads, chains designed for use with Chainomatic balances are suitable. For higher loads, inexpensive jewelry chains were used. They were found to be accurate to ± 0.5 percent of their maximum load at any point. It is believed that this error could be reduced by the use of specially

A, Successive loading and recovery cycles for a wool fiber, stretched 35 percent in water five times; *B*, relaxation curve for a single wool fiber. The fiber was stretched to 10-percent elongation in the wet state, and then allowed to relax.

made chains. It has been found convenient to use several heavy chains in parallel for testing strong fibers.

Figure 4 shows a load-elongation curve obtained from the apparatus for a wool fiber elongated at a constant rate in water. The fiber was

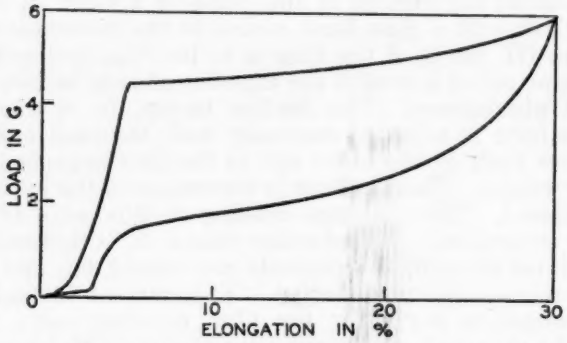

FIGURE 5.—*Hysteresis loop obtained by tracing the curve of figure 4.*

elongated to 30 percent, and then returned to zero elongation. The point of reversal of the platform motor is marked by the arrow. It should be noted from this figure that the load increases in a downward direction, and also that the kymograph drum does not reverse

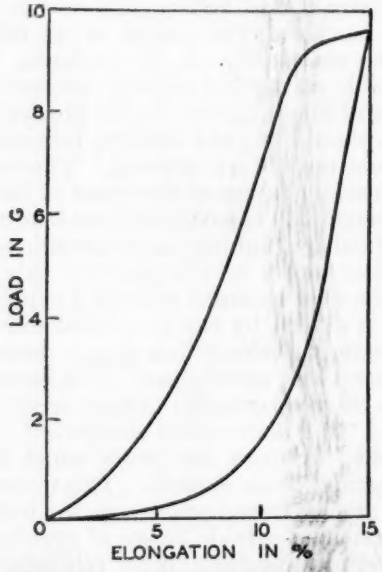

FIGURE 7.—*Loading and recovery cycle for a single filament of drawn nylon (2.3 denier), which was stretched in the wet state to 15-percent elongation and then returned to its initial length.*

when the fiber is returned to zero elongation. The conventional type of hysteresis loop, with load plotted against elongation, can be obtained from the curve of figure 4 by folding the record paper along a vertical axis passing through the arrow, and then inverting the paper. A tracing made in this way is shown in figure 5.

A series of load-elongation and recovery cycles on a single wool fiber extended in the wet condition is shown in figure 6 (*A*). In this experiment, the fiber was elongated 35 percent, after which the platform was reversed. When the fiber had returned to zero elongation, the cycle was repeated, etc. The figure shows the progressive decrease in the load developed by stretching the fiber to 35 percent in successive cycles. For this type of experiment, continuous unidirectional rotation of the kymograph motor is advantageous, since the record would be very confusing after a number of cycles if the curve returned to the origin.

Figure 6 (*B*) shows a relaxation curve for a single wool fiber. The fiber was stretched to 10 percent in the wet state, at which point (marked by the arrow) the platform was stopped. The machine then automatically recorded the decay of tension in the fiber as a function of time. Figure 7 shows a loading and recovery cycle for a single

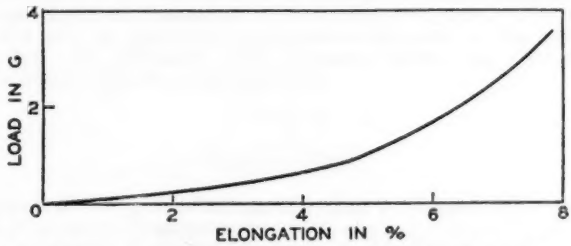

FIGURE 8.—*Load-elongation curve to failure for a single fiber of Sea Island cotton stretched in the wet state.*

filament of drawn nylon (2.3 denier), which was stretched in the wet state to 15-percent elongation, and then returned. The curve was traced from the record made by the machine, in the manner described above. A load-elongation curve to the break on a single fiber of Sea Island cotton elongated in the wet state is shown in figure 8.

For all the examples described above, the platform was lowered at a constant speed of 0.169 in. per minute, and the gear reduction between the controlled motor (which lowers the chain) and the sprockets of the Chainomatic column was 500:1.

IV. REFERENCES

[1] S. G. Barker, Wool Quality, His Majesty's Stationery Office, London (1931).
[2] R. L. Steinberger, Textile Research **4,** 207 (1934).
[3] G. Osumi and E. Kato, Rayon Textile Monthly **19,** 381, 436, 494 (1938).
[4] A. M. Sookne and M. Harris, J. Research NBS **19,** 535 (1937) RP1043; Am. Dyestuff Reptr. **26,** 659 (1937).
[5] R. H. Muller and R. L. Garman, Ind. Eng. Chem., Anal. Ed., **10,** 436 (1938).
[6] Private communication from Dr. Garman.

WASHINGTON, February 15, 1943.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1547

Part of Journal of Research of the National Bureau of Standards, Volume 31, July 1943

RING STRUCTURES AND MUTAROTATIONS OF THE MODIFICATIONS OF *D*-GALACTURONIC ACID

By Horace S. Isbell and Harriet L. Frush

ABSTRACT

A study of the two crystalline modifications of galacturonic acid has been made with the object of determining their ring structure. The results show that they are a pair of alpha-beta pyranoses analogous to the alpha and beta galactopyranoses. On oxidation with bromine water, the two modifications yield optically active lactones of mucic acid.

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1. COMPARISON OF THE MUTAROTATIONS OF α- AND β-*D*-GALACTURONIC ACID WITH THOSE OF α- AND β-*D*-GALACTOPYRANOSE

Galacturonic acid, the chief constituent of all pectin material, is one of the most abundant and important sugar derivatives. It is a substituted aldose having the *D*-galactose configuration, and as such it is capable of existing in various modifications. In fact, two crystalline modifications are known, one of which has been assumed to be an open chain modification and the other a pyranose [1].[1] Inasmuch as an open chain modification of a free sugar is unique in the field of carbohydrate chemistry, and since it has been found that substances having the galactose configuration give rise to complex mutarotation reactions indicating the presence of both pyranose and furanose modifications in the equilibrium mixture [2, 3], it seemed desirable to investigate the modifications of galacturonic acid and to study the changes which occur when they are dissolved in water.

One of the crystalline forms of galacturonic acid, a monohydrate originally designated "alpha", is reported to give an initial specific rotation of $+98°$ and an equilibrium value of $+50.9°$; the other, an

[1] Figures in brackets indicate the literature references at the end of this paper.

anhydrous form commonly designated "beta", is reported to give an initial specific rotation of +27° and an equilibrium value of +55.3°. Calculated on the anhydrous basis, the same equilibrium value is approached by either the alpha or the beta modification, and either form can be obtained from the equilibrium solution by appropriate treatment. An aldehydohydrate structure was assigned to the alpha modification by Ehrlich and Schubert [1] on the basis that the molecule of water is very tenaciously held, and that the compound develops color quickly with Schiff's fuchsine-aldehyde reagent, whereas the beta modification develops color slowly. Since the positive aldehyde test requires only a very small amount of the open-chain modification, and this might be formed from the cyclic modification after dissolution in water, the evidence for the assignment of the open-chain structure is not sufficient, and, in fact, some investigators have tacitly assumed an alpha pyranose structure [4]. The anhydrous modification has been considered to be a beta pyranose, largely because it is less dextrorotatory than the monohydrate, and because most sugars crystallize as pyranose modifications.

In publications from this laboratory it has been emphasized that substances having like configurations for the atoms comprising the pyranose ring have similar properties [2, 3, 5]. It therefore seemed of interest to compare the mutarotation curves of the modifications of galacturonic acid with those of α- and β-*D*-galactopyranose. The two modifications of galacturonic acid were prepared and the mutarotation measurements reported in table 1 were made.

For comparison, curves representing the mutarotations of the two modifications of galacturonic acid, and of galactose are given in figures 1 and 2. An examination of the figures reveals that the curves for the two modifications of galacturonic acid are analogous to the curves for the two modifications of galactose. Thus, the mutarotations of the alpha modifications are characterized by an initial rapid change, whereas the mutarotations of the beta modifications are characterized by an initial retardation. Inasmuch as an initial rapid change is characteristic of the α-galactopyranose structure, and an initial retaration is characteristic of the β-galactopyranose structure, the comparisons support the classification of the two modifications of galacturonic acid as an alpha-beta pyranose pair.

II. BROMINE OXIDATION OF THE MODIFICATIONS OF GALACTURONIC ACID

In previous investigations a method was developed for studying the modifications of the sugars present in aqueous solution by means of bromine oxidation in conjunction with mutarotation measurements [6]. Since the several modifications of the same sugar react with bromine at widely different rates, and usually the oxidation reactions are rapid in comparison with the mutarotation reactions, the proportions of the various modifications can be calculated from the reaction rates. Moreover, a study of the reaction products reveals additional information. Pyranoses on oxidation yield delta lactones, whereas furanoses yield gamma lactones. Thus the pyranose modifications of galacturonic acid should give the delta lactone of mucic acid by the reaction of equation I, the furanose modification should give the

TABLE 1.—*α-D-Galacturonic acid hydrate*

4 g per 100 ml at 20° C, read in a 2-dm tube.
$^{\circ}S = 10.66 \times 10^{-.0148t} + 2.44 \times 10^{-.16t} + 12.34$.*
$[\alpha]_D^{20} = 44.83 \times 10^{-.0148t} + 10.26 \times 10^{-.16t} + 51.90$.
$[\alpha]_D^{20} = +107.0$ (initial), $+51.9$ (equilibrium).

Time	Observed reading	k_1+k_2	m_1	Deviation	m_3
Minutes	° *S*				
0				(2.44)	
1.3	+24.05			1.51	
1.7	+23.66	0.0368		1.26	0.20
2.4	+23.22	.0290		1.06	.14
3.6	+22.46	.0257		0.69	.15
4.2	+23.13	.0268		.55	.15
4.9	+21.77	.0261		.41	.16
7.1	+20.88	.0236		.17	.16
8.8	+20.30	.0224		.06	.19
17.4	+18.23	.0185			
21.7	+17.43	.0177	0.0148		
25.9	+16.72	.0174	.0151		
30.2	+16.14	.0169	.0149		
60.0	+13.74	.0157	.0146		
∞	+12.34				
Average			0.0148		0.16

β-*D*-GALACTURONIC ACID

4 g per 100 ml at 20° C, read in a 2-dm tube.
$^{\circ}S = -7.23 \times 10^{-.0148t} + 1.41 \times 10^{-.13t} + 12.88$.
$[\alpha]_D^{20} = -31.84 \times 10^{-.0148t} + 6.21 \times 10^{-.13t} + 56.72$.
$[\alpha]_D^{20} = +31.1$ (initial), $+56.7$ (equilibrium).

Time	Observed reading	k_1+k_2	m_1	Deviation	m_3
Minutes	° *S*				
0				(1.41)	
1.9	+6.90			0.80	
2.6	+6.94	0.0041		.68	0.10
3.6	+6.98	.0034		.50	.12
4.8	+7.08	.0046		.34	.13
6.3	+7.22	.0054		.17	.15
7.8	+7.44	.0070		.10	.15
12.7	+8.19	.0098			
19.3	+9.13	.0116	0.0147		
23.5	+9.61	.0121	.0145		
27.1	+10.00	.0126	.0147		
30.5	+10.34	.0130	.0150		
34.9	+10.68	.0132	.0148		
55.1	+11.80	.0140	.0150		
∞	+12.88				
Average			0.0148		0.13

* The method for calculating the equation and the constants is described in detail on page 156 of [6].

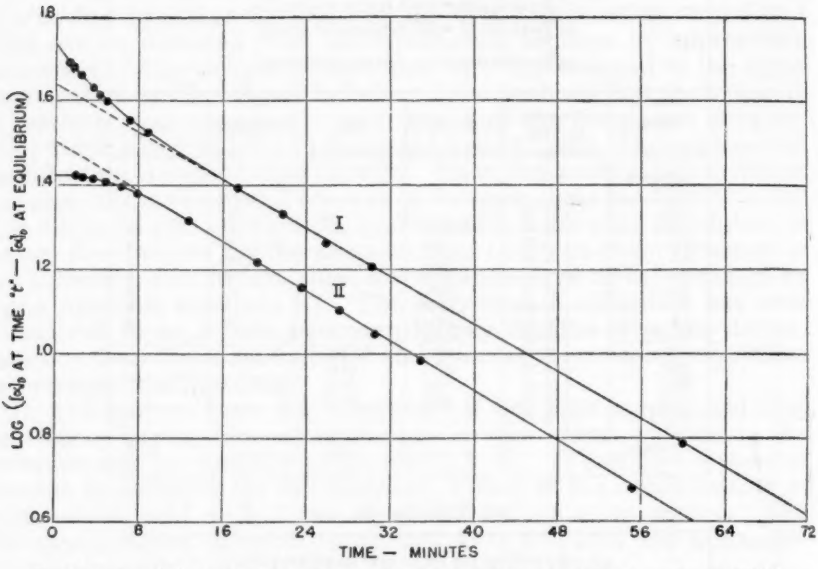


FIGURE 1.—*Mutarotations of α- and β-D-galacturonic acid in water at 20°C.*

I, α-*D*-galacturonic acid; II, β-*D*-galacturonic acid.

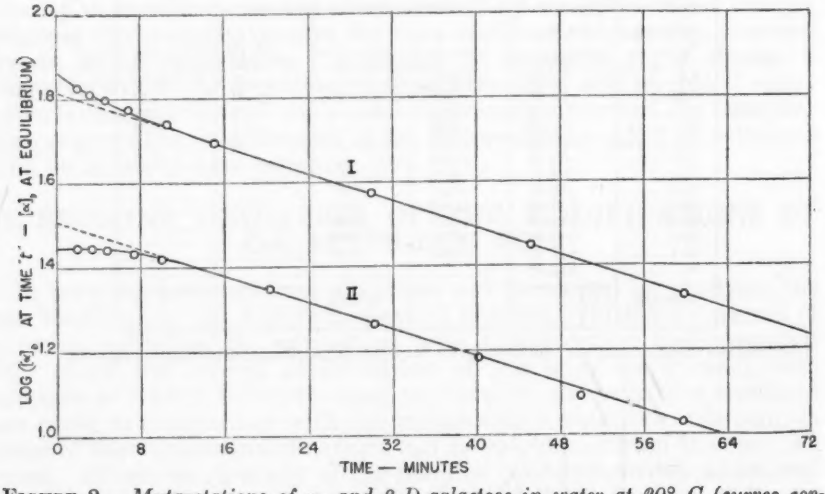
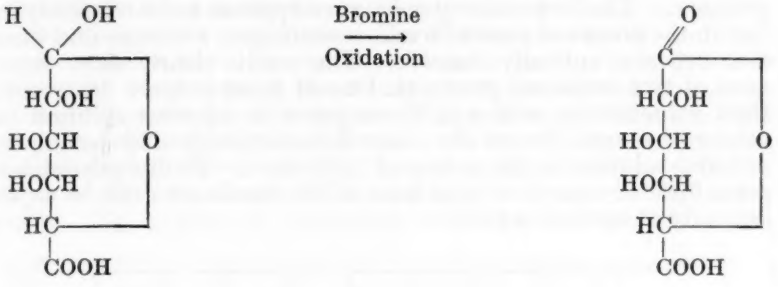


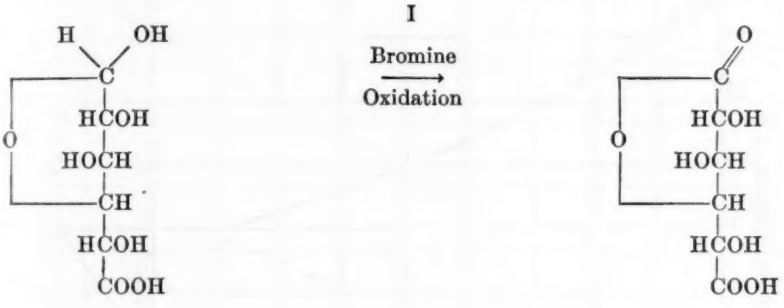
FIGURE 2.—*Mutarotations of α- and β-D-galactose in water at 20° C (curves constructed from data given in [2]).*

I, α-*D*-galactose; II, β-*D*-galactose.

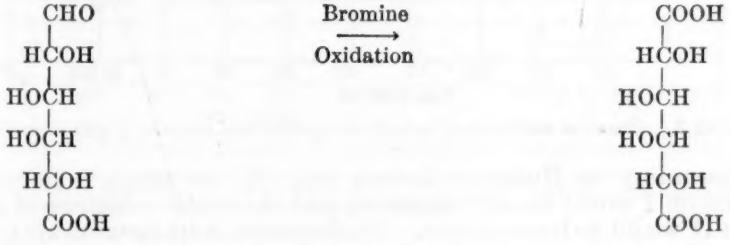
gamma lactone by the reaction of equation II and the open chain modification should give mucic acid by the reaction of equation III.



I



II



III

Mucic acid is a *meso* compound, and hence on lactone formation gives rise to a racemic mixture because there is equal probability that either end of the molecule may be involved in ring formation. However, the delta and gamma lactones of mucic acid, obtained by oxidation of the pyranose and furanose modifications of galacturonic acid, should be optically active since a *meso* configuration is not present during lactone formation. The formation of optically active lactones has now been observed experimentally. The production of these unique substances is striking evidence that the ring modifications of galacturonic acid are oxidized with bromine directly to the lactones of mucic acid without the intermediate formation either of the open-chain modification of galacturonic acid, or of free mucic acid.

The formation of these optically active lactones is shown by the changes in optical rotation (fig. 3) which occur during and after the oxidation of an equilibrium solution of galacturonic acid. When

bromine is added to the solution the optical rotation increases; the initial increase in dextrorotation is followed by a fairly rapid change in the opposite direction with the result that the solution becomes levorotatory. The levorotatory substance appears to be relatively stable, but in the course of several weeks it undergoes a change and the solution becomes optically inactive. The results clearly show the existence of two oxidation products: One of these is more dextrorotatory than galacturonic acid and decomposes in aqueous solution in the course of several hours; the other is levorotatory and decomposes in aqueous solution in the course of may days. Hydrolysis with bases gives optically inactive salts from which mucic acid can be separated in nearly quantitative yield.

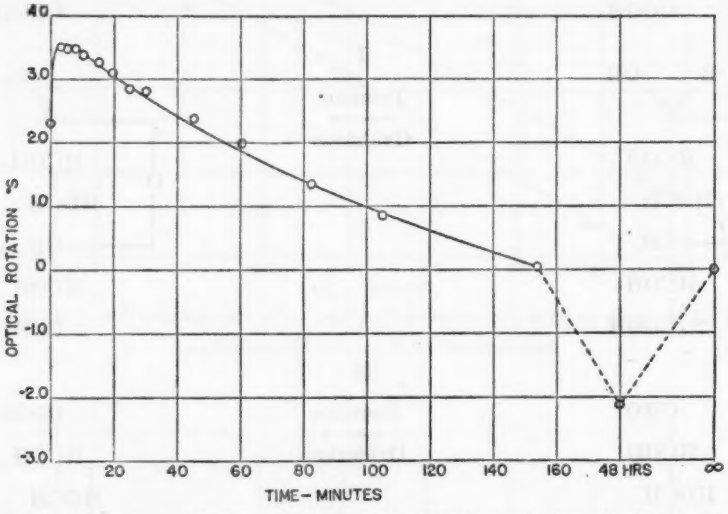


FIGURE 3.—*Bromine oxidation of a buffered equilibrium solution of galacturonic acid.*

According to Hudson's lactone rule [7] the mucic δ-lactone of equation I would be dextrorotatory and the mucic γ-lactone of equation II would be levorotatory. Furthermore, delta lactones are hydrolyzed by water at room temperature in the course of several hours, whereas gamma lactones are hydrolyzed much more slowly [8]. It is therefore apparent that the dextrorotatory product obtained experimentally is the unknown optically active delta lactone of mucic acid, whereas the levorotatory product is the unknown optically active gamma lactone. The oxidation of an equilibrium solution of galacturonic acid therefore follows equations I and II, and the solution contains both pyranose and furanose modifications. The existence of the furanose modifications in the equilibrium solution is not surprising because we have already demonstrated that the mutarotation involves a fast reaction analogous to the pyranose-furanose interconversion that is characteristic of substances having the galactose structure.

Measurements made after oxidation of freshly prepared solutions of the alpha and the beta modifications of galacturonic acid likewise show the production of both delta and gamma lactones of mucic acid, a fact which indicates that the oxidation of the freshly dissolved

crystalline isomer is complicated by a relatively fast pyranose-furanose inter conversion. Although a strictly quantitative method for determining the delta and gamma lactones of mucic acid is not available, the approximate amounts can be estimated from the changes in optical rotation which take place when the lactones are hydrolyzed. Our measurements have shown that the delta lactone is hydrolyzed completely by treatment of the solution with barium carbonate at room temperature for five minutes, and that under such conditions the gamma lactone is only slightly affected. Hence the amount of delta lactone can be estimated from the optical rotations observed before and after a short treatment of the oxidation mixture with barium carbonate. By prolonged treatment with barium carbonate the

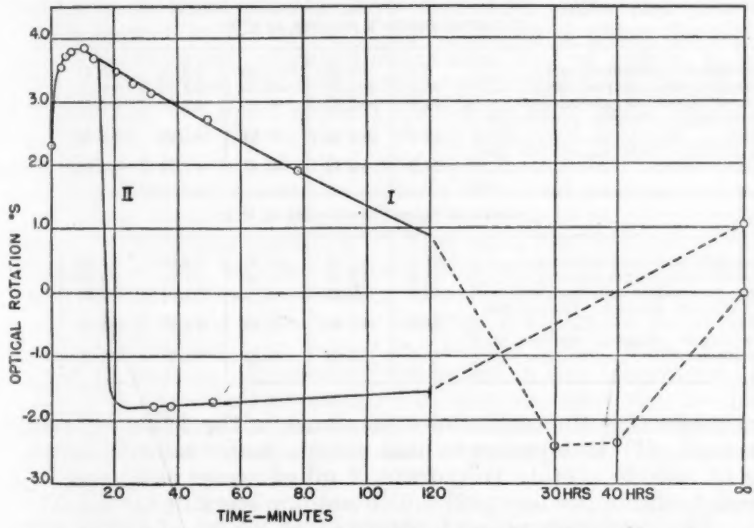


FIGURE 4.—*Bromine oxidation of freshly dissolved β-D-galacturonic acid.*

I, Changes in optical rotation of a buffered solution containing *β-D*-galacturonic acid and bromine; II, changes in optical rotation of a sample which was oxidized for 15 minutes. The bromine was then removed, and the delta lactone hydrolyzed by short treatment with $BaCO_3$.

gamma lactone is also hydrolyzed. Hence this lactone can be estimated from the difference in the optical rotations measured after short, and after prolonged treatment with barium carbonate. Furthermore, since the final product, barium mucate, is optically inactive, the optical rotation of the solution obtained after hydrolysis of the lactones is proportional to the amount of unoxidized galacturonic acid. The changes in optical rotation which occur during and after the oxidation of a freshly prepared solution of β-galacturonic acid are given in figure 4 together with the changes which occur when the oxidation is interrupted and the product treated with barium carbonate. Additional results obtained by the oxidation of freshly prepared solutions of α- and β-galacturonic acid, and sodium galacturonate, and of equilibrium solutions of these substances are reported in table 2.||

TABLE 2.—*Bromine oxidation of D-galacturonic acid in solutions buffered with acetic acid and sodium acetate*

Material oxidized	Percentage of sample oxidized	Optical rotation			Differences in optical rotations	
		Before treatment with $BaCO_3$	After short treatment with $BaCO_3$	After long treatment with $BaCO_3$	Before and after short treatment with $BaCO_3$ (δ-lactone)	Before and after long treatment with $BaCO_3$ (γ-lactone)
1	2	3	4	5	6	7
OXIDATION PERIOD 5 MINUTES AT 0° C						
Crystalline α-galacturonic acid	6.1	+2.35	+1.90	+2.16	+0.45	−0.26
Crystalline β-galacturonic acid	35.2	+2.41	−0.09	+1.49	+2.50	−1.58
Crystalline sodium galacturonate	34.3	+2.43	−.20	+1.51	+2.63	−1.71
Equilibrium solution, galacturonic acid	22.6	+2.41	+.65	+1.78	+1.76	−1.13
Equilibrium solution, sodium galacturonate	24.9	+2.49	+.53	+1.73	+1.96	−1.20
OXIDATION PERIOD 15 MINUTES AT 0° C						
Crystalline α-galacturonic acid	18.8	+2.25	+0.93	+1.88	+1.32	−0.95
Crystalline β-galacturonic acid	54.8	+3.43	−1.80	+1.04	+5.23	−2.84
Crystalline sodium galacturonate	56.3	+3.21	−1.70	+1.01	+4.91	−2.71
Equilibrium solution, galacturonic acid	44.8	+2.80	−0.89	+1.27	+3.69	−2.16
Equilibrium solution, sodium galacturonate	47.4	+3.04	−.98	+1.21	+4.02	−2.19

In conducting the oxidation measurements the following solutions were used: (1) An aqueous sodium acetate buffer solution containing 60 g of sodium acetate trihydrate, 2 ml of acetic acid, and 74 g of sodium bromide per liter; (2) 0.5 N sodium acetate; (3) 0.5 *N* acetic acid. The oxidation reagent consisted of 25 ml of buffer solution (1), 1 ml of bromide, and 5 ml of either (2) or (3), depending on whether the free acid or the sodium salt was to be studied. The buffered bromine solution was cooled to 0° C and 0.0025 mole of the galacturonic acid, or salt, in 20 ml of ice water was added. Time was measured from the moment the solutions were mixed. In the experiments on the freshly dissolved acid, or salt, the material was mixed with the ice water immediately before the addition to the oxidation reagent; in the measurements on the equilibrium solutions the material was added to 20 ml of water and allowed to stand 18 hours before addition to the oxidation reagent. The reaction mixture in a glass-stoppered flask was immersed in ice and water, and shaken for a period of either 5 or 15 minutes, after which interval the reaction was stopped by shaking the solution for a few minutes with 10 ml of linseed oil dissolved in 20 ml of benzene. The mixture was allowed to separate, and the aqueous layer was withdrawn with a pipette and filtered.

A portion of the filtrate was transferred to a polariscope tube and the optical rotation was read at various times. The rotation at a definite time (20 minutes) was obtained by plotting these readings against time and is recorded in column 3 of table 2.

A second portion of the filtrate was mixed for 5 minutes at 20° C with an excess of barium carbonate. The unreacted barium carbonate was separated by filtration and the optical rotation of the filtrate was read as soon as possible. The values so obtained are recorded in column 4 of table 2. The change in optical rotation produced by short treatment with barium carbonate and recorded in column 6 is a measure of the amount of delta lactone.

A third portion of the filtrate was hydrolyzed by reaction with barium carbonate over a period of 10 days. The optical rotation after this treatment, recorded in column 5 of table 2, represents the amount of unoxidized galacturonic acid [2] and the difference in the optical rotations of columns 4 and 5, recorded in column 7, is a measure of the amount of gamma lactone.

The results of these studies show that both delta and gamma lactones are formed in the course of the oxidation of either the alpha or the beta modification of galacturonic acid, and of sodium galacturonate. In each case the delta lactone predominates in the oxidation product, but the exact amount cannot be ascertained from the optical rotations until the rotations of the unknown optically active delta and gamma lactones of mucic acid have been determined. The presence of substantial quantities of both delta and gamma lactones in the oxidation products indicates the occurrence of rapid pyranose-furanose interconversion reactions. These rapid reactions complicate the evaluation of the separate velocity constants for the oxidation reactions. Nevertheless, the amounts of oxidation of the two modifications of galacturonic acid under strictly comparable conditions clearly reveal that the beta isomer is oxidized much more rapidly than the alpha isomer. Prior work conducted in this laboratory has shown that beta pyranoses are oxidized by bromine more rapidly than alpha pyranoses. Hence the relative rates of oxidation for the alpha and beta modifications of galacturonic acid support their classification as alpha and beta pyranoses.

The oxidation of freshly dissolved sodium galacturonate follows essentially the same course as that of freshly dissolved β-galacturonic acid. It may be concluded therefore that the sodium salt contains the beta pyranose modification of galacturonic acid.

The oxidation of the freshly dissolved alpha or beta modification of galacturonic acid presumably takes place in two ways: The first course is by direct oxidation of the substance used; the second is by conversion to other modifications through the mutarotation reaction, and the subsequent oxidation of these. The predominance of one or the other of the two courses depends on the experimental conditions. When the conditions are such that the mutarotation reaction is rapid in comparison with the bromine oxidation, the apparent rates of oxidation for all modifications approach the rate characteristic of the equilibrium solution. In the present investigation, bromine oxidations of galacturonic acid were conducted with a barium carbonate buffer, as well as with the acetate buffer for which results are reported in table 2. It was found, however, that when barium carbonate was used as buffer, equilibrium of the modifications of galacturonic acid

[2] The optical rotation of galacturonic acid or of sodium galacturonate in the sodium acetate-acetic acid medium used above is +2.3° at the concentration employed, and is not changed appreciably by treatment with barium carbonate.

was established so quickly that the apparent rates of oxidation for both modifications and for the equilibrium solution were alike. Furthermore, the sensitivity of the delta lactone of mucic acid to hydrolysis by barium carbonate interfered in the analytical method. These results are in contrast to those obtained with the simple sugars for which barium carbonate was found to be a satisfactory buffer. [9]. The sensitivity of the pyranose modifications of galacturonic acid to basic catalysts seems analogous to the sensitivity of the corresponding delta lactone of mucic acid to hydrolysis by barium carbonate.

The fact that the mutarotation reactions of galacturonic acid are rapid in solutions buffered with barium carbonate and carbon dioxide was shown by the following experiment.

One gram of *α-D*-galacturonic acid was dissolved in 25 ml of water saturated with carbon dioxide, and the solution was shaken for 3 minutes at 20° C with 2 g of barium carbonate. The mixture was filtered, and the optical rotation of the filtrate was read from time to time. The rotation first observed 7 minutes after dissolution of the acid, remained constant over a period of several hours. This experiment shows that treatment of *α*-galacturonic acid with barium carbonate at 20° C results in an equilibrium mixture within a period of 7 minutes. The rapid establishment of equilibrium explains why, in the presence of barium carbonate, the various modifications of galacturonic acid are oxidized at about the same rate and yield essentially the same oxidation products.

III. PREPARATION OF *α-D*-GALACTURONIC ACID MONOHYDRATE

Crude galacturonic acid prepared from citrus pectic acid by the method of Mottern and Cole [10] was extracted with methyl alcohol as described by Pigman [11]. After removal of the methyl alcohol by concentration under reduced pressure, a crystalline massecuite was obtained, which was diluted with glacial acetic acid to the point of saturation. After standing for about 1 day, the crystals were separated and washed with aqueous acetic acid The crystalline galacturonic acid monohydrate thus obtained was recrystallized by dissolving it in an equal weight of hot water, treating with a small quantity of a decolorizing carbon, filtering and adding acetic acid to the point of saturation. The crystals which formed in the course of several hours were separated and recrystallized slowly, with constant motion, from a concentrated aqueous solution. The crystals obtained after several days were collected on a filter and washed with aqueous acetic acid. After drying over sodium hydroxide to constant weight, the alpha galacturonic acid monohydrate gave an initial rotation $[\alpha]_D^{20}=+107.0$ (H_2O, C=4), an equilibrium rotation $[\alpha]_D^{20}=+51.9$, and the mutarotation represented by curve I of figure 1. The initial optical rotation of the hydrate is higher than that previously reported (+97.9); the equilibrium rotation of +51.9 is in fair agreement with that reported by Pigman (+51.5), but it is considerably higher than the rotation reported by Ehrlich and Schubert (+50.9). The specific rotations expressed on the anhydrous basis are $+116.9\rightarrow+56.7$.

IV. PREPARATION OF *β-D*-GALACTURONIC ACID

The beta modification of galacturonic acid used in the present investigation was originally prepared from the alpha isomer by crys-

tallization from absolute alcohol essentially as described by Ehrlich and Schubert [1]. However, we found that it could be obtained more simply by crystallization from hot glacial acetic acid, in the following manner:

Ten grams of pure finely powdered α-*D*-galacturonic acid monohydrate is added to 80 ml of glacial acetic acid and the mixture is heated to boiling with stirring. Before the boiling point of the acetic acid is reached the galacturonic acid goes into solution and shortly thereafter the crystalline beta modification separates. The mixture is then cooled to approximately 50° C and the crystals are separated and washed with glacial acetic acid. The product thus obtained is largely the beta modification but additional treatment with hot glacial acetic acid is necessary in order to obtain pure β-*D*-galacturonic acid. After five successive 15-minute digestions with boiling acetic acid, the material, dried over sodium hydroxide, gave an initial rotation $[\alpha]_D^{20}=+31.1$ (H_2O, C=4), an equilibrium rotation $[\alpha]_D^{20}=+56.7$ and the mutarotation represented by curve II of figure 1.

V. COMPARISON OF THE MOLECULAR ROTATIONS OF α- AND β-*D*-GALACTURONIC ACID WITH THOSE OF α- AND β-*D*-GALACTOPYRANOSE

Comparisons of the optical rotations of certain acetylated derivatives of galactose and galacturonic acid made by Goebel and Reeves [12] revealed a parallelism, with regular differences which were ascribed to the effect of the substituent groups on the partial rotation of carbon 5. As may be observed from the data given in table 3, the molecular rotations of galacturonic acid, galactose, and their respective glycosides likewise show certain parallelisms. In general, the molecular rotations in the galactose series are more dextro than those in the galacturonic acid series. The differences may be ascribed to the effect of the carboxyl attached to carbon 5 in contrast to the effect of the primary alcoholic group in the sugar.

According to the principle of isorotation [13], the molecular rotation of an alpha pyranose may be considered as $+A+B$, and that of the corresponding beta pyranose as $-A+B$, where A is the optical rotation attributed to the glycosidic carbon, and B is the optical rotation of the remaining asymmetric carbons. The sum of the molecular rotations of the alpha and beta isomers is $2B$ and the difference is $2A$. The value of $2A$ (16,650) for the modifications of galacturonic acid is in accord with the value of $2A$ (17,650) for the alpha and beta modifications of *D*-galactose. This agreement substantiates the classification of the two modifications of galacturonic acid as an alpha-beta pair of cyclic isomers.

TABLE 3.—*Comparison of molecular rotations*

	$[M]_D$	$2A$	$2B$
α-*D*-Galacturonic acid.H_2O	+22, 700	16, 650	28, 750
β-*D*-Galacturonic acid	+6, 050		
Methyl α-*D*-galacturonide.$2H_2O$ [4]	+31, 150	40, 100	22, 200
Methyl β-*D*-galacturonide.H_2O [14]	−8, 950		
α-*D*-Galactose [2]	+27, 150	17, 650	36, 650
β-*D*-Galactose [2]	+9, 500		
Methyl α-*D*-galactopyranoside.H_2O [15]	+38, 050	38, 050	38, 050
Methyl β-*D*-galactopyranoside [16]	0		

VI. SUMMARY

1. A study of the mutarotation reactions of α-*D*-galacturonic acid monohydrate and of β-*D*-galacturonic acid has been made. The mutarotation of α-*D*-galacturonic acid monohydrate follows much the same course as the mutarotation of α-*D*-galactopyranose, and that of β-*D*-galacturonic acid follows much the same course as that of β-*D*-galactopyranose. For α-*D*-galacturonic acid hydrate $[\alpha]_D^{20} = 44.83\times10^{-.0148t}+10.26\times10^{-.16t}+51.90$, corresponding to an initial specific rotation of +107.0, and an equilibrium value of +51.9. For β-*D*-galacturonic acid $[\alpha]_D^{20} = -31.84\times10^{-.0148t}+6.21\times10^{-.13t}+56.72$, corresponding to an initial specific rotation of +31.1, and an equilibrium value of +56.7.

2. In addition to the parallelism in the course of the mutarotation reactions, the molecular rotations and other properties likewise indicate that α-*D*-galacturonic acid monohydrate and β-*D*-galacturonic acid are an alpha-beta pyranose pair analogous to α- and β-*D*-galactopyranose.

3. Both α- and β-*D*-galacturonic acid on oxidation with bromine water in acid solution yield optically active delta and gamma lactones of mucic acid. The formation of optically active lactones is evidence that the ring forms of galacturonic acid are oxidized without the intermediate formation of either the open-chain modification of galacturonic acid, or of free mucic acid, and the formation of both delta and gamma lactones is evidence of a relatively rapid pyranose-furanose interconversion of galacturonic acid.

4. The beta modification of galacturonic acid is oxidized by bromine more rapidly than the alpha isomer.

5. An improved method for converting α-*D*-galacturonic acid monohydrate to β-*D*-galacturonic acid is described.

6. Oxidation measurements show that sodium galacturonate is a salt of β-*D*-galacturonic acid.

VII. REFERENCES

[1] F. Ehrlich and F. Schubert, Ber. deut. chem. ges. **62,** 1974 (1929).
[2] H. S. Isbell, J. Research NBS **18,** 505 (1937) RP990.
[3] H. S. Isbell and W. W. Pigman, J. Research NBS **20,** 773 (1938) RP1104.
[4] S. Morell and K. P. Link, J. Biol. Chem. **100,** 385 (1933).
[5] H. S. Isbell and H. L. Frush, J. Research NBS **24,** 125 (1940) RP1274.
[6] H. S. Isbell and W. W. Pigman, J. Research NBS **18,** 141 (1937) RP969.
[7] C. S. Hudson, J. Am. Chem. Soc. **32,** 338 (1910).
[8] P. A. Levene and H. S. Simms, J. Biol. Chem. **65,** 31 (1925).
[9] H. S. Isbell, BS J. Research 8, 615 (1932) RP441.
[10] H. H. Mottern and H. L. Cole, J. Am. Chem. Soc. **61,** 2701 (1939).
[11] W. W. Pigman, J. Research NBS **25,** 301 (1940) RP1325.
[12] W. F. Goebel and R. E. Reeves, J. Biol. Chem. **124,** 207 (1938).
[13] C. S. Hudson, BS Sci. Pap. **21,** 241 (1926) S533. See also F. J. Bates and Associates, Circular National Bureau of Standards C440, p. 432 (1942).
[14] S. Morell, L. Baur, and K. P. Link, J. Biol. Chem. **110,** 719 (1935).
[15] E. Fischer, Ber. deut. chem. Ges. **28,** 1155 (1895).
[16] C. N. Riiber, J. Minsaas, and R. T. Lyche, J. Chem. Soc. **1929,** 2173.

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TEN-YEAR TESTS ON COMMERCIAL MASONRY CEMENTS

By R. L. Blaine

ABSTRACT

In an investigation of the properties of 41 commercial masonry cements reported in 1934, additional specimens were made for tests at a later age. Two-inch mortar cubes made of these cements were tested in compression after both water and air storage for 10 years. Mortar bar specimens were measured for linear change after storage in water for 10 years.

The compressive strengths of the 1:3 (cement to standard sand) mortar cubes varied from 200 to 6,000 lb/in.^{2} at 10 years. Variables, such as type of cement, amount of mixing water, ratio of cement to sand, gradation of sand, as well as storage conditions are shown to affect not only the strength at 10 years but also the gain in strength between 28 days and 10 years.

The length measurements indicate a trend of greater expansion with greater magnesia content of the cement.

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I. INTRODUCTION

At the time of the investigation of the properties of 41 commercial masonry cements, reported in 1934,[1] comparable information relative to compressive strengths and volume change of masonry cement mortars after extended storage was not available. This report, in supplement to the original, concerns the compressive-strength tests and the expansion measurements of the masonry cement mortars at 10 years. The identification numbers of the cements are the same as in the original report. However, the chemical analyses of cements 38 and 39 were published in the original report in inverse order, and cognizance should be taken of this in the study of the relation of chemical composition to volume change.

[1] J. S. Rogers and R. L. Blaine, *Investigation of commercial masonry cements*, J. Research NBS **13**, 811 (1934) RP746.

In the discussion of strengths of the mortars, the cements were classified into groups according to their general nature, as presented in the original report, namely:

P=Largely portland cement;
PL=Portland cement and hydrated lime mixtures;
PM=Portland cement mixed with unidentified materials;
PN=Portland cement and natural cement mixtures;
N=Natural cement;
S=Large amount of slag;
U=Not identified;
HL=Hydraulic or hydrated lime;

II. TESTS

Two-inch cubes were made of the mortars X, X–1, and Y, the composition and preparation of which are described in the original report. A summary of the compositions is given here to facilitate comparisons.

Mortar:	*Proportions*
X	1:3, by weight, cement: standard (20–30) Ottawa sand.[2]
X–1	1:2:1, by weight, cement: standard (20–30) Ottawa sand: fine testing sand.[3]
Y	1:2:1, by volume, cement: standard (20–30) Ottawa sand: fine testing sand.[3]

In all the mortars, the amount of water required for normal consistency (a flow of 100 to 115 on the standard 10-inch flow table) was used. In addition, 1 percent more and 1 percent less water (based on the dry weight of cement and sand) than that required for normal flow was used for both mortars X and X–1.

The sand and cement were mixed dry. Then water was added and mixing continued for 5 minutes. The mortars were allowed to stand 14½ minutes and were again mixed for one-half minute.

The 2-inch cubes made from the above mortars were stored in the damp closet for 2 days in the molds, after which the cubes were removed from the molds and stored in the damp closet for an additional 5 days. The specimens were then stored in water, and after 7 days half of the specimens were removed and stored in laboratory air until tested.

The 2-inch mortar cubes were tested in compression at 7 days, 28 days, 3 months, 1 year, and 10 years. Three specimens were tested at each age after both water and air storage.

Length measurements were made every week for 1 month, then every month for 1 year, and then at 10 years on the 1- by 1- by 8-inch mortar X bars described in the original report. These specimens, after 7 days of storage in the damp closet, were stored in water until measured. The companion bars, stored in air, were not measured, inasmuch as the glass plates that formed the ends of the bars had been broken off in many instances.

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[2] Federal Specification SS–C–158a, Cements, Hydraulic; General Specifications (Methods for Sampling, Inspection, and Testing), paragraph F–4l (1).
[3] Federal Specification SS–C–158a, Cements, Hydraulic; General Specifications (Methods for Sampling, Inspection, and Testing),paragraph F–4m (1).

III. RESULTS

1. COMPRESSIVE STRENGTH

(a) DRY VERSUS WET STORAGE

A plot of the results of the 10-year compressive-strength tests of the 2-inch cubes made of the 1:3, by weight, cement to standard (20–30) Ottawa sand mortar of normal consistency is presented in figure 1. The strengths of the water-stored specimens are plotted against those of the air-stored specimens.

It may be noted in figure 1 that all the cements classified in the natural (N) or slag (S) groups had greater compressive strength after

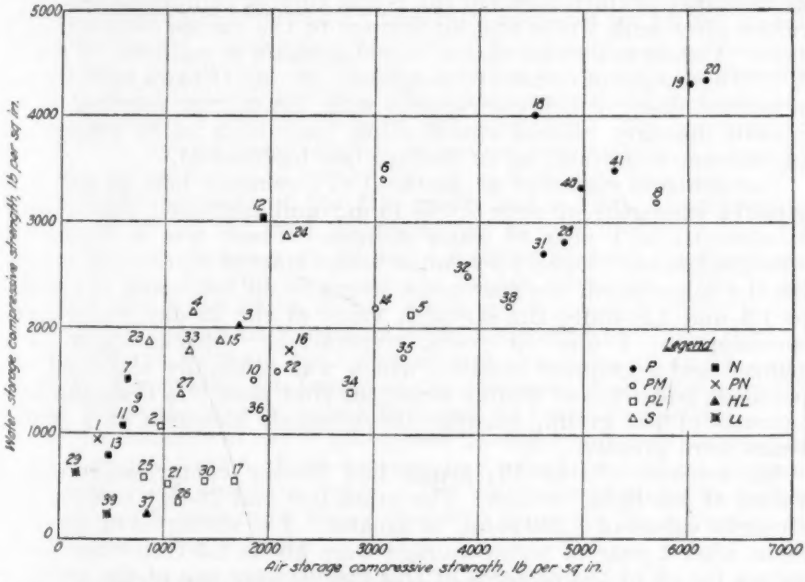

FIGURE 1.—*Relation of the compressive strengths after water and air storage for 10 years of 2-inch cubes made of 1:3, by weight, cement to standard (20–30) sand mortar of normal flow.*

water storage than after air storage. All the cements of the portland (P) group, 8 of 10 of the cements of the portland-with-unidentified-materials (PM) group, and 7 of 8 of the portland cement-hydrated lime (PL) group had greater strength after air storage than after water storage. The pairs of cements of the types portland-natural (PN), hydraulic or hydrated lime (HL), and unidentified (U) and one of each type in which the greater strength was obtained in water storage, whereas with the other cement of each type the greater strength was obtained with air storage. It may also be noted from figure 1 that 2 of 2 U, 1 of 2 PN, 1 of 2 HL, 3 of 4 N, 1 of 6 S, 1 of 10 PM, and 2 of 8 PL cements had compressive strengths of less than 1,000 lb/in.^{2} after 10 years of air storage. After 10 years of water storage, 2 of 2 U, 1 of 2 PN, 1 of 4 N, and 5 of 8 PL cements had compressive strengths less than 1,000 lb/in.^{2} Only six of the cements had compressive strengths of 1,000 lb/in.^{2} or less with both storage conditions. After

10 years of water storage, 17 of the 41 cements had compressive strengths of 2,000 lb/in.^{2} or greater, and 18 cements had compressive strengths of 2,000 lb/in.^{2} or greater after air storage. Fourteen of the cements had 2,000 lb/in.^{2} or greater compressive strength with both storage conditions.

(b) INCREASE IN STRENGTH AT LATER AGES

Specifications [4] for masonry cements require compressive-strength tests at only 7 and 28 days. However, it is known that some types of cement have different rates of strength increase when exposed to damp or to dry conditions, and also that some types of masonry cement increase in strength and others do not. Therefore an analysis was made of the relation of the 1- and 10-year compressive-strength values after both water and air storage to the values obtained at 28 days. Unless otherwise stated, the discussion is confined to mortar X (1:3 by weight of cement to standards, (20–30) Ottawa sand mortar, of normal flow), which corresponds with the mortar required in the present masonry cement specification tests both as to proportions and storage conditions up to 28 days (see footnote 4).

The cements classified as portland (P) cements had 28-day compressive strengths of over 2,000 lb/in.^{2} and increased only slightly in strength in 1 year of water storage. There was a decrease in strength between 1 and 10 years of water storage with every cement. On the other hand, the specimens stored in air increased in strength to 1.4 and 1.8 times the strength value of the 28-day water-stored specimens at 1 and 10 years, respectively. Specimens made of cement 18, a grappier cement, which was originally classified as a portland cement, had 28-day strengths that were less than the other cements of the group, whereas the strength increases at 1 and 10 years were greater.

Six cements of the PL group had 28-day compressive-strength values of 500 lb/in.^{2} or less. The other two had 28-day compressive-strength values of 1,200 lb/in.^{2} or greater. The strengths of the specimens after 1 year of water storage were about 1.5 times the 28-day values for all of the cements of this group; only one of the group increased slightly in strength from 1 to 10 years, whereas six indicated a slight decrease in strength. The compressive strength after 1 year of air storage was about 2.0 times, and at 10 years, 2.7 times the values obtained for the 28-day water-stored specimens.

Nine of ten cements of the PM group had 28-day compressive strengths of about 1,000 lb/in.^{2} or greater. The cements of this group had compressive strengths after 1 year of water storage of 1.4 times the values obtained for the 28-day water-stored specimens. Only 2 of the 10 cements had further strength increases between the period of 1 and 10 years of water storage, and 7 of the 10 cements had slight strength decreases in the same period. After air storage for 1 and 10 years, the respective compressive-strength values were 1.6 and 1.8 times the 28-day strength values of water-stored specimens. Cement 9 had a 28-day compressive strength of 650 lb/in.^{2}, and the compressive strength of the specimens stored in air was only slightly higher at 1 year, whereas at 10 years the value had decreased slightly. One other cement in this group had a slight strength decrease between 1 and 10 years in air storage.

[4] Federal Specification for Cement; Masonry SS-C-181b, and Standard Specifications for Masonry Cement ASTM Designation C-91-40.

Five of six of the slag (S) cements had 28-day compressive-strength values of 500 to 1,000 lb/in.^{2}. After storage in water the strength values were 2.0 and 2.8 times the 28-day values at 1 and 10 years, respectively. In air storage, however, the 1-year compressive-strength values were about 2.0 times the 28-day values, and only one of the six cements had an increase in strength between 1 and 10 years, whereas four of the six decreased in strength in the air storage. One of the six cements of this group decreased in strength between 1 and 10 years in both wet and dry storage.

Of the two cements of the PN group, one of the cements had a compressive strength of 170 lb/in.^{2} after 28 days of water storage, but increased to 2.3 and 5.7 times the 28-day value at 1 and 10 years respectively, when stored in water. After 10 years of storage in air the compressive strength was 2.3 times the values of the 28-day water-stored specimens. The other cement of this group had a compressive strength of 750 lb/in.^{2} at 28 days, and the value at 1 year of water storage was 2.5 times this value. The compressive strength decreased slightly between 1 and 10 years of water storage. The compressive strength at 1 and 10 years of air storage were, respectively, 2.1 and 2.9 times the values obtained on the 28-day water-stored specimens.

One of the cements of the HL group had a 28-day compressive strength of 400 lb/in.^{2}, and the respective 1- and 10-year values for water-stored specimens were 3.4 and 4.6 times, whereas the air-stored specimens were 2.4 and 3.9 times the 28-day strengths. The other cement of this group had a 28-day compressive strength of 220 lb/in.^{2} Water-stored specimens were only slightly stronger at 1 year than at 28 days, and at 10 years the strength was the same as at 28 days. The compressive-strength values of the air-stored specimens were 2.3 and 3.7 times the 28-day values at 1 and 10 years, respectively.

The two cements of the U group had 28-day compressive strengths of less than 100 lb/in.^{2} Both cements had a high percentage increase in strength when stored in water. The compressive-strength values of the air-stored specimens were 1.9 and 2.3 times the 28-day values at 1 and 10 years, respectively.

(c) EFFECT OF PROPORTIONS ON STRENGTH INCREASES

A comparison was made of the percentage strength increases at 1 and 10 years of both water- and air-stored specimens of mortar X made of standard (20–30) sand and mortar X–1 made of the graded sand. With many cements there was only a slight, if any, difference in the strength increase of the two mortars, whereas with other cements there were appreciable differences. However, no well-established trend was observed. It was noted in comparing these two mortars that mortar X-1 had, in almost every instance, greater 10-year compressive-strength values than the corresponding mortar X.

A comparison was also made of the ratio of compressive strengths at 10 years and 28 days of mortars X and Y proportioned 1:3 by weight and by volume, respectively. The leaner mortar specimens had the greater strength increases between 28 days and 10 years of water storage in 27 of 33 cements. These were divided as follows: 7 of 7 PL, 8 of 10 PM, 6 of 6 S, 1 of 4 N, 1 of 2 PN, 2 of 2 HL, and 2 of 2 U. However, with air storage, the leaner specimens did not have so great a strength increase as the 1:3 by weight mortar specimens. This was true in 30 of 33 cements, and these were apportioned as follows: 6 of 7 PL, 9 of 10 PM, 4 of 4 N, 5 of 6 S, 2 of 2 PN, 2 of 2 HL, and

2 of 2 U. No trend was noted with the portland cements, possibly because the 1:3 by weight and by volume were more nearly the same.

In table 1 is presented the effect of both water content and mortar composition on the strength ratios of five of the types of cement. The values presented are the averages of all the cements of each group. It may be noted that in considering any one type of cement the percentage compressive-strength increase was very nearly the same regardless of water content.

TABLE 1.—*Ratio of compressive strength values*

Mortar	Consistency [a]	Age and storage: 10 yr water / 28 day water	Age and storage: 10 yr air / 28 day water	Mortar	Consistency [a]	Age and storage: 10 yr water / 28 day water	Age and storage: 10 yr air / 28 day water
CEMENT P							
X	N−1	1.1	1.5	X−1	N−1	1.2	1.8
X	N	1.0	1.6	X−1	N	1.0	1.6
X	N+1	1.1	1.7	X−1	N+1	1.0	1.6
				Y	N	1.1	1.8
CEMENT PM							
X	N−1	1.3	1.8	X−1	N−1	1.4	1.8
X	N	1.3	1.8	X−1	N	1.3	2.0
X	N+1	1.4	1.9	X−1	N+1	1.5	2.1
				Y	N	1.7	1.4
CEMENT PL							
X	N−1	1.3	2.8	X−1	N−1	1.4	2.7
X	N	1.4	2.7	X−1	N	1.5	2.8
X	N+1	1.3	2.8	X−1	N+1	1.5	2.9
				Y	N	1.7	2.3
CEMENT N							
X	N−1	3.4	2.1	X−1	N−1	3.1	2.4
X	N	4.0	2.3	X−1	N	3.4	2.3
X	N+1	4.3	2.2	X−1	N+1	3.6	2.1
				Y	N	3.2	1.8
CEMENT S							
X	N−1	2.6	1.8	X−1	N−1	2.4	1.6
X	N	2.8	1.8	X−1	N	2.7	1.8
X	N+1	3.0	1.6	X−1	N+1	2.5	1.7
				Y	N	3.6	1.2

[a] N = Mortar of normal flow; N−1 = 1 percent less water than that required for normal flow, N+1 = 1 percent more water than that required for normal flow.

2. LENGTH MEASUREMENTS

The results of the length measurements on the bars made of mortar X of normal consistency that were stored in water for 10 years are presented in figure 2. The percentage increase in length is plotted against the percentage of magnesia in the cement. There appears to be a definite trend of greater expansions with mortars made of cements of higher magnesia content. Although the mortar bars made from cements having less than 4 percent of magnesia, all had

linear expansions of less than 0.04 percent in 10 years, and those made from four of the cements having a high magnesia content had linear expansions of from 0.265 to 0.808 percent; nevertheless, mortars

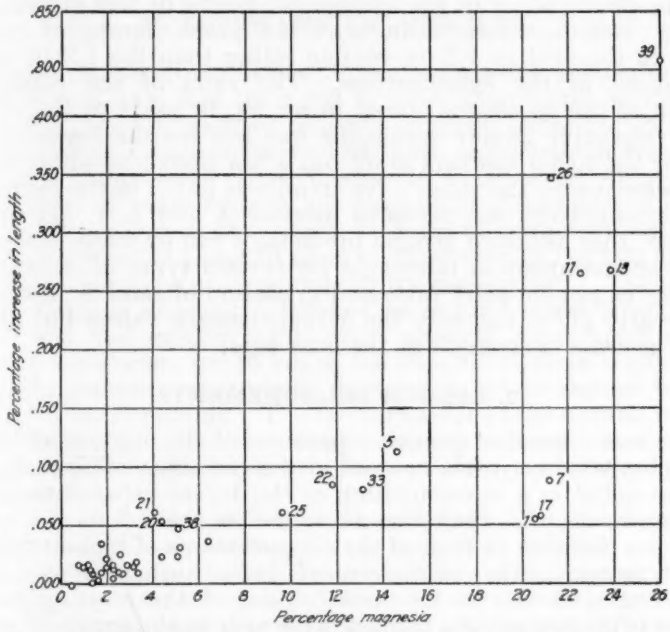

FIGURE 2.—*Relation between the magnesia content of the cement and the percentage increase in length in 10 years of water storage of 1- by 1- by 8-inch bars made of 1:3, by weight, cement to standard (20–30) sand mortar of normal flow.*

made from three of the cements having a high magnesia content expanded only from 0.05 to 0.09 percent.

IV. DISCUSSION

1. COMPRESSIVE STRENGTH

It is impracticable to require specification strength tests at periods greater than 28 days. However, the 28-day results are not indicative of the strengths that may be expected, unless something is known of the composition of the cement. Consideration should also be given, especially with the low-strength cements, to the conditions under which the mortar is to be used. For example, many of the cements which were originally classified as portland cement-hydrated lime mixtures had relatively low compressive strengths even after 10 years of water storage. On the other hand, some of the natural cements had low compressive strengths after 10 years of air storage. It is realized that the storage conditions of this investigation are not the same as those under which the mortars are used, but cognizance should be taken of the fact that some of the cements do not have a great increase in compressive strength after 28 days under certain storage conditions. Hence, in a general specification for masonry cement, the 28-day strength requirements should be set sufficiently

high, and too much dependence should not be placed on subsequently expected strength increases. Many of the mortars made of these cements had decreases in strength values between 1 and 10 years with one or the other of the storage conditions of this investigation.

Many manufacturers recommend the proportioning of masonry mortar in the field as 1:3 by volume rather than the 1:3 by weight, as required in the specifications. The ratio of the compressive strength of the specimens stored in air for 10 years to the strength of the respective 28-day specimens was less for the leaner mortars than for the richer mortars in all but a few instances where the two ratios were nearly the same. No trend was noted in the comparison of the strength-increase ratios of mortars X and X–1. It appears, therefore, that although general predictions can be made of strengths of mortar specimens at later ages for certain types of cement, such variables as cement-sand ratio and gradation of sand in the mortar may greatly affect not only the actual-strength values but also the rate of increase in strength at the later ages.

2. LENGTH MEASUREMENTS

There was a trend of greater expansions of the mortars at 10 years with the greater magnesia content of the cements. This same trend was also noted in a reexamination of the 1-year expansions of these same specimens. It may also be noted in table 3 of the original report (see footnote 1) that, of the seven cements of highest magnesia content, mortars of five of the cements broke during the wetting and drying cycles of one of the tests. Most of the mortars made of cements of high magnesia content were also in the group of mortars failing in 10 or less cycles of freezing and thawing.

The presence of unhydrated, or free, magnesia in cementitious materials has long been recognized as an element contributing to unsoundness because of the expansion concomitant with the hydration of the oxide to the hydroxide form. As a safeguard, portland cement specifications limit the total magnesia, although the magnesia, as determined by chemical analysis, may not all be the unhydrated MgO. The autoclave expansion test has also been developed as a further safeguard of soundness.

Masonry cements are sometimes made by the addition of either slag, hydrated dolomitic lime, or finely ground dolomitic limestone to a portland cement or other material for purposes of plasticizing or diluting the cement. Accordingly, in many cases the magnesium compounds may not be of the unhydrated form, e. g., some may be in the form of carbonate from the limestone, and some may be completely hydrated, since completely hydrated limes are now available. Therefore, inasmuch as the character of the magnesium compound is significant, it would be unfair, with masonry cements, to limit the percentage of total "MgO" content as determined by chemical analysis.

In this investigation, mortars of four of the seven cements of high "MgO" content expanded considerably more than the other three of this group, indicating that the total "MgO" content, as determined by chemical analysis, is not a criterion of expansion.

The determination of the free, or unhydrated, magnesia in mixtures such as masonry cements would be impractical, if not impossible, and

it therefore appears that the only method to safeguard against excessive expansions would be the adoption of an autoclave expansion test such as is required in portland cement specifications.

V. SUMMARY OF RESULTS

The compressive strengths of 1:3 masonry cement to standard sand mortars varied from less than 200 to more than 6,000 lb/in.^{2} at 10 years. The mortars made of cements originally classified as largely portland, portland-plus-unknown additions, and portland-lime mixes had greater compressive strength after 10 years of air storage than after 10 years of water storage; the mortars of these types of cement had very little increase or a slight decrease in compressive strength between the period of 1 and 10 years of water storage but had appreciable strength increases in air storage for the same period. The mortars made of cements originally classified as natural cements or largely slag cements had greater compressive strength after water storage than after air storage for 10 years; the mortars of these cements had appreciable compressive-strength increases in water storage between the 1- and 10-year periods. The mortars made of the natural cements increased only slightly in compressive strength, whereas those made of the slag cements decreased slightly between the 1- and 10-year periods of air storage.

Mortars made of the graded sand maintained a higher compressive strength than mortars made with the standard (20–30) sand with most of the cements at the 10-year test period. At 10 years the leaner mortar Y had greater strength increase with water storage and smaller increase with air storage than the standard 1:3 mortar compared with the respective 28-day compressive-strength values. The percentage of water used in preparing the mortars did not alter to a great extent the ratio of the compressive-strength increases between 28 days and 10 years The necessity for an adequate 28-day compressive-strength requirement was discussed.

The linear expansion of mortar specimens in 10 years varied from 0 to 0.808 percent. There was a definite trend of greater expansion with greater magnesia content of the cement. All mortar specimens made of cements having less than 4 percent of magnesia had linear expansions of less than 0.04 percent during 10 years of water storage. Conversely, mortars made of four of seven of the cements with the highest magnesia contents had expansions greater than 0.25 percent.

WASHINGTON, March 27, 1943.

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MATHEMATICAL TABLES

Attention is invited to a series of publications prepared by the *Project for the Computation of Mathematical Tables* conducted by the Federal Works Agency, Work Projects Administration for the City of New York under the sponsorship of the National Bureau of Standards. The tables which have been made available through the National Bureau of Standards are listed below.

There is included in this list a publication on the hypergeometric and Legendre functions (MT15), prepared by the Bureau.

MT1. TABLE OF THE FIRST TEN POWERS OF THE INTEGERS FROM 1 TO 1000:

(1938) VIII+80 pages; heavy paper cover. 50 cents.

MT2. TABLES OF THE EXPONENTIAL FUNCTION e^x.

The ranges and intervals of the argument and the number of decimal places in the entries are given below:

Range of x	Interval of x	Decimals given
—2.5000 to 1.0000	0.0001	18
1.0000 to 2.5000	.0001	15
2.500 to 5.000	.001	15
5.00 to 10.00	.01	12

(1939) XV+535 pages; bound in buckram, $2.00.

MT3. TABLES OF CIRCULAR AND HYPERBOLIC SINES AND COSINES FOR RADIAN ARGUMENTS:

Contains 9 decimal place values of sin x, cos x, sinh x and cosh x for x (in radians) ranging from 0 to 2 at intervals of 0.0001.
(1939) XVII+405 pages; bound in buckram, $2.00.

MT4. TABLES OF SINES AND COSINES FOR RADIAN ARGUMENTS:

Contains 8 decimal place values of sines and cosines for radian arguments ranging from 0 to 25 at intervals of 0.001.
(1940) XXIX+275 pages; bound in buckram, $2.00.

MT5. TABLES OF SINE, COSINE, AND EXPONENTIAL INTEGRALS, VOLUME I:

Values of these functions to 9 places of decimals from 0 to 2 at intervals of 0.0001.
(1940) XXVI+444 pages; bound in buckram, $2.00.

MT6. TABLES OF SINE, COSINE, AND EXPONENTIAL INTEGRALS, VOLUME II:

Values of these functions to 9, 10, or 11 significant figures from 0 to 10 at intervals of 0.001, with auxiliary tables.
(1940) XXXVII+225 pages; bound in buckram, $2.00.

MT7. TABLE OF NATURAL LOGARITHMS, VOLUME I:

Logarithms of the integers from 1 to 50,000 to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, $2.00.

MT8. TABLES OF PROBABILITY FUNCTIONS, VOLUME I:

Values of these functions to 15 places of decimals from 0 to 1 at intervals of 0.0001 and from 1 to 5.6 at intervals of 0.001.
(1941) XXVIII+302 pages; bound in buckram, $2.00.

[Continued on p. 4 of cover]

[Continued from p. 3 of cover]

MT9. TABLE OF NATURAL LOGARITHMS, VOLUME II:

Logarithms of the integers from 50,000 to 100,000 to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, $2.00.

MT10. TABLE OF NATURAL LOGARITHMS, VOLUME III:

Logarithms of the decimal numbers from 0.0001 to 5.0000, to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, $2.00.

MT11. TABLES OF THE MOMENTS OF INERTIA AND SECTION MODULI OF ORDINARY ANGLES, CHANNELS, AND BULB ANGELS WITH CERTAIN PLATE COMBINATIONS:
(1941) XIII+197 pages; bound in green cloth, $2.00.

MT12. TABLE OF NATURAL LOGARITHMS, VOLUME IV:

Logarithms of the decimal numbers from 5.0000 to 10.0000, to 16 places of decimals.
(1941) XXII+506 pages; bound in buckram, $2.00.

MT13. TABLE OF SINE AND COSINE INTEGRALS FOR ARGUMENTS FROM 10 TO 100:
(1942) XXXII+185 pages; bound in buckram, $2.00.

MT14. TABLES OF PROBABILITY FUNCTIONS, VOLUME II:

Values of these functions to 15 places of decimals from 0 to 1 at intervals of 0.0001 and from 1 to 7.8 at intervals of 0.001.
(1942) XXI+344 pages; bound in buckram, $2.00.

MT15. The hypergeometric and Legendre functions with applications to integral equations of potential theory. By Chester Snow, National Bureau of Standards. Reproduced from original handwritten manuscript.

(1942) VII+319 pages; bound in heavy paper cover, $2.00.

MT16. TABLE OF ARC TAN X:

Table of inverse tangents for positive values of the angle in radians. Second central differences are included for all entries.

Range of x	Interval between successive arguments
0 to 7	0.001
7 to 50	.01
50 to 300	.1
300 to 2,000	1
2,000 to 10,000	10

(1942) XXV+169 pages; bound in buckram, $2.00.

MT17. Miscellaneous Physical Tables:
Planck's radiation functions (Originally published in the Journal of the Optical Society of America, February 1940); and
Electronic functions.
(1941) VI+58 pages; bound in buckram, $1.50.

MT18. Table of the Zeros of the Legendre Polynomials of Order 1–16 and the Weight Coefficients for Gauss's Mechanical Quardrature Formula.
(Reprinted from Bull. Amer. Mathemical Society, October 1942.)
5 pages. 25 cents.

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A mailing list is maintained for those who desire to receive announcements regarding new tables as they become available.